Certified that the work described in this thesis is the original work of Mr. Baij Nath Khanna., done under my super[illegible]

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P R E F A C E.

The thesis deals with the emission spectra of chlorine, bismuth monochloride and bismuth monobromide molecules and is divided into five chapters.

Chapters I and II deal with the emission spectrum of chlorine excited in the presence of argon. Two band systems were obtained in the region 2600 - 2390A and 2365 - 2239A. As many as about 200 bands are obtained in the system 2600 - 2390A as against only 24 bands obtained by Cameron and Elliott in the excitation by active nitrogen. The system 2365 - 2239A is new. Both the systems are analysed for the first time and the vibrational constants given. These systems are found to be analogous to the 2950 - 2670A and 2660 - 2590A systems of bromine. Both the systems are photographed with a 21-ft grating spectrograph.

Chapter III deals with the experimental data and the vibrational analysis of the band system 6170 - 4220A obtained by exciting $BiCl_3$ vapour with an uncondensed transformer discharge. As many as 390 bands are obtained in the present experiments as against only 140 bands obtained by earlier workers either in absorption or in emission by arc flame. The earlier work on this molecule in absorption was carried out in a tube open to atmosphere while the earlier work in emission was done in flame open to atmosphere. A vibrational analysis of the bands obtained is given which is supported by the probable isotopic shifts observed.

It was found that the constants obtained by Morgan with the addition of the cubic term for the upper state explain practically all the bands observed.

Chapter IV deals with the rotational structure of four bands and the probable electronic terms involved in the band system 6170 - 4220A of BiCl. The rotational structure of the BiCl molecule has been observed and studied for the first time. The rotational analysis gives the rotational constants, the vibrational-rotational-interaction cnnstants as well as the internuclear distance for the upper and lower electronic states. The study of the rotational structure along with a detailed discussion of the electronic configuration enabled the determination of the probable electronic transition in the band system.

Chapter V deals with the emission spectrum of BiBr obtained by exciting $BiBr_3$ with an uncondensed transformer discharge. In the band system 5710 - 4650A as many as about 240 bands are obtained in the present experiments as against only 61 bands recorded by Morgan in absorption. All the bands obtained have been analysed and the probable dissociation energies of the upper and lower states are obtained.

The different chapters in the thesis are written in a form suitable for publication. They will be submitted separately for publication during the next few weeks. Each chapter contains a separate introduction and a separate abstract. A general introduction is not therefore given.

All the work described in this thesis has been carried out by me in the Department of Physics, Muslim University, Aligarh under the guidance of Dr. Putcha Venkateswarlu. I wish to express my indebtedness and thanks to him for his guidance and encouragement during the course of the work. I am thankful to Professor P.S. Gill and the University Authorities for giving me permission to work in the Department of Physics and for giving me a University Research Scholarship. Sincere thanks are due to Dr. Ram Din Verma for his constant encouragement and inspiration during the course of the work. Thanks are also due to other different colleagues and friends Messrs Y. Venkateswar Rao, P.R.K.Sarma, A. Sundar Rajan, K.V.L.N.Sastry, D. Ramchandra Rao and B.D.Nageswar Rao for their encouragement and Mr. Ajit Singh, the glass blower, for his help.

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C O N T E N T S.

CHAPTER I.

Emission spectrum of chlorine excited in the presence of ARGON.

Part I.

The Band system in the region 2600-2390A.

Emission Spectrum of Chlorine Excited in The Presence of Argon.

Part I: The Band system in the Region 2600 - 2390A^{o}.

Abstract.

The spectrum of chlorine excited in the presence of argon has been photographed with a 21-ft grating spectrograph in the first order. Two band systems in the regions 2600-2390A and 2365-2239A are observed. The wavelengths and the wavenumbers of all the bands in the system 2600 - 2390A are given. The vibrational scheme along with the corresponding Frank-Condon parabola is also given. The analysis suggests that the lower state of the system is the $^{3}\pi(O_u^+)$ state established by Elliott at 1658 cm^{-1} and that the upper state is at 57773 cm^{-1}. The vibrational constants obtained are $\omega_e' = 246.6$ cm^{-1}, $\omega_e'x_e' = 0.615$ cm^{-1}, $\omega_e'' = 255.2$ cm^{-1}, $\omega_e''x_e'' = 5.5$ cm^{-1}, $\omega_e''y_e'' = 0.0155$ cm^{-1} and $\omega_e''z_e'' = 0.00115$ cm^{-1}.

Introduction.

The emission spectrum of chlorine excited by means of a transformer discharge or a high frequency electrodeless discharge is known to show a set of discrete bands in the region 6000 - 3900A and groups of continua in the region 3100 - 1850A. After a study of the rotational structure of some of the discrete bands in the visible region, Elliott and Cameron [1-2] attributed the discrete bands to the Cl_2^+ molecule. They were, however, able to put only half of the bands observed into a vibrational scheme. Haranath and Rao[3] are of the opinion that these discrete bands belong to four sub-systems. The discrete bands are being worked out in this laboratory with the higher orders of a 21-ft grating spectrograph and the results obtained will be reported separately. The groups of continua were explained by Venkateswarlu[4] as arising due to transitions from upper stable states to different

unstable states dissociating into $^2P + {}^2P$ normal chlorine atoms.

Cameron and Elliott[5] excited chlorine in the presence of active nitrogen and reported 24 narrow diffuse bands superposing the original chlorine continuum in the region 2580-2400A.

Iodine and bromine when excited without the presence of a foreign gas are known to show groups of broad diffuse bands [6-9] which are due to transitions from upper stable states to lower unstable states dissociating into $^2P + {}^2P$ neutral atoms. It is also known that when these gases are excited in the presence of argon, the groups of diffuse bands fade away and new discrete band systems show up. Four such band systems were obtained earlier in iodine[10-11] and three recently in bromine[12-14]. Because of these interesting results in iodine and bromine, one is naturally tempted to expect similar results in chlorine. The spectrum obtained by exciting chlorine in the presence of argon is, therefore, studied and the results obtained are discussed in this chapter.

Experimental Details.

Chlorine vapur was excited in the presence of argon by an uncondensed transformer discharge. The discharge tube, having nickel electrodes, was 40 cms in length and 0.8 cms in diameter and was made of pyrex glass. One end of it was fitted with a quartz window and at the other end a side tube containing anhydrous cupric

chloride was attached. The discharge tube was fed with the chlorine gas prepared by heating anhydrous cupric chloride with an electric furnace to the temperature of nearly 300°C. Argon marked spectrally pure was obtained from Oxygen Acetylene Company;

It was found that as the pressure of argon in the discharge tube ~~is~~ was increased, original discrete bands of chlorine at 6000-3900A and the group of diffuse bands at 3100-1850 A ~~go~~ went down in intensity and new spectrum appeared. By adjusting the relative pressures of argon and chlorine inside the discharge tube, it was possible to eliminate the original spectrum (except for faint traces at the intense portions) and obtain only the new spectrum. When long exposures were needed, it was found necessary to cool the discharge tube with a table fan and flush the tube with fresh samples of chlorine and argon after every 6 hours, so as to avoid the continuum that overlaps the new systems.

Two band systems are obtained. One is a strong and extensive system in the region 2600-2390 A and the other is a weak system in the region 2305-2239 A. It was found that these systems could be well developed by adjusting the pressures of the constituent gases such that the discharge was bluish-white in colour. It may be mentioned that the relative pressures ~~are~~ were not measured in these experiments, but it ~~is~~ was estimated that the pressure of argon ~~is~~ was many times higher than that of chlorine.

FIGURE I(B).

The enlargement of the 2600-2390A system of chlorine obtained in the first order of a 21-ft grating spectrograph.

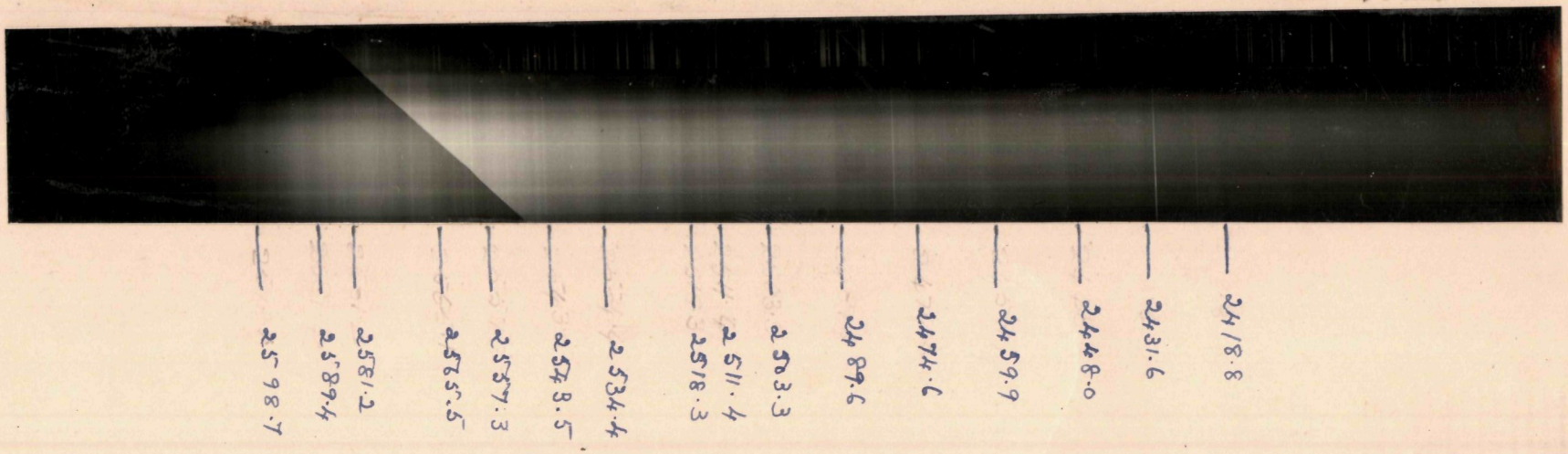
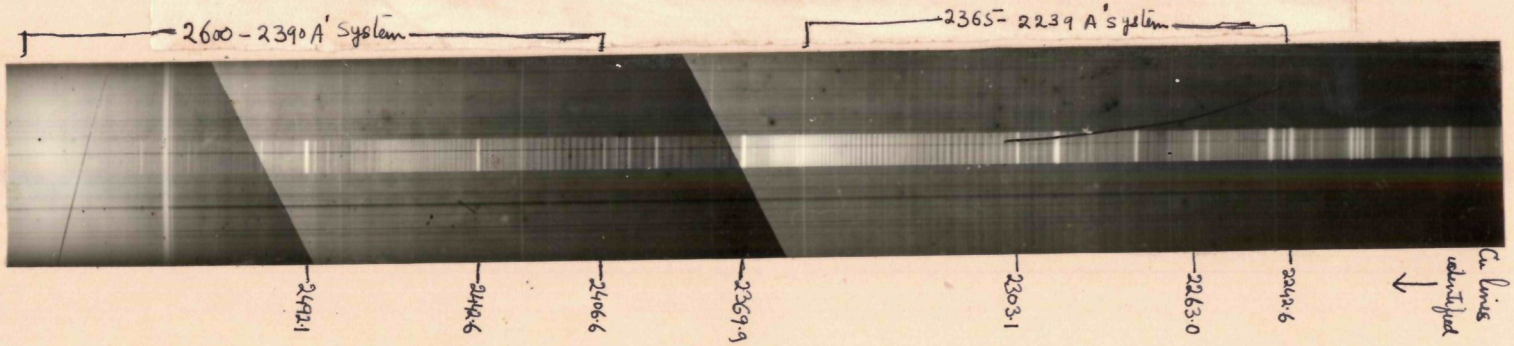


FIGURE I(A).

The enlargement of the 2600-2390A and 2365-2239A systems of chlorine excited in the presence of Argon taken with Hilger Medium Quartz spectrograph.



The spectrum was photographed first on a Hilger Medium Quartz Spectrograph and then on a 21-ft. grating spectrograph in the first order. Fig I shows the enlargements of the spectrum obtained with the 21-ft. grating spectrograph. The band system 2600-2390 A only will be discussed in this chapter. The bands of this system in general appear to be degraded towards longer wavelengths. There are also a number of bands for which the degradation is not clear. The wavelengths and wavenumbers of the band heads are given in table I along with their estimated relative intensities. As the band heads are not very sharp, the error in the measurements of their positions may be about ± 4 cm^{-1}. The wavelengths of the 24 narrow diffuse bands obtained with a low dispersion instrument by Cameron and Elliott[5] in this region by exciting chlorine in the presence of active nitrogen are also included in the table for comparison. It appears likely that in the experiments of Cameron and Elliott, the new extensive band system was just beginning to show up and the continua were beginning to go down in intensity. The occurrence of this system in the excitation by active nitrogen suggests, as pointed out by Cameron and Elliott, that the emitter of the system is very likely Cl_2 and not Cl_2^+. This system appears to be analogous to the 3450-3040 A system of iodine[11] and 2950-2670 A system of bromine[12].

Vibrational Analysis of the band system 2600-2390A.

The Deslandres scheme for the band system in the

TABLE I.

Wavelengths, wavenumbers and relative intensities of the bands in the system 2600 - 2390A.

Cameron & Elliott	Present experiments			Cameron & Elliott	Present experiments		
λair	I	λair	ν vac	λair	I	λair	ν vac
	1	2615.5	38222		1	2590.1	38597
	1	2614.9	38231		4	2589.4	38607
	1	2614.3	38240		1	2588.5	38621
	1	2613.5	38251		1	2586.2	38655
	0	2608.7	38321		2	2585.1	38672
	1	2607.4	38341		4	2584.5	38681
	1	2606.7	38351		1	2583.7	38693
	1	2605.7	38366		0	2583.3	38699
	2	2605.0	38376		2	2582.2	38715
	2	2603.2	38402				
	1	2601.7	38425		4	2581.9	38720
	0	2601.2	38432	2581.4	5	2581.2	38730
	0	2600.4	38440		5	2580.8	38736
	2	2599.9	38452		1	2579.9	38750
	2	2598.7	38469		5	2578.4	38772
	0	2596.8	38497	2577.3	0	2577.6	38784
	2	2598.0	38480		2	2577.0	38793
	2	2595.3	38520		5	2575.5	38816
	1	2595.1	38523		4	2574.8	38826
	1	2592.5	38561		2	2573.7	38843
	1	2591.0	38584		4	2572.7	38858

Table I (cont'd.)

Cameron & Elliott	Present experiments		Cameron & Elliott	Present experiments		
λair	I	λair	νvac	λair	I	λair	νvac
	3	2572.2	38866		7	2543.5	39304
	3	2571.4	38878		2	2542.7	39317
	1	2569.3	38909		2	2541.5	39335
	10	2568.6	38920		1	2540.0	39358
2567.9	3	2568.3	38924		2	2538.8	39377
	2	2566.9	38946	2537.2	3	2537.6	39396
	3	2566.0	38960		1	2537.0	39405
	7	2565.1	38973		3	2536.0	39420
	4	2563.5	38998		1	2535.2	39433
	3	2561.4	39029		4	2534.4	39445
2559.9	6	2560.5	39043		1	2533.9	39453
	4	2558.7	39071		2	2532.4	39476
	4	2558.1	39080		2	2531.7	39487
	8	2557.3	39092		1	2530.2	39511
	2	2555.6	39118	2529.2	1	2529.6	39520
2553.9	2	2554.0	39143		3	2528.9	39531
	3	2552.9	39159		4	2528.1	39544
	3	2551.7	39177		2	2527.5	39553
	6	2550.5	39196		4	2526.4	39570
	1	2549.8	39207		1	2525.1	39591
	1	2549.3	39215		1	2524.6	39598
	4	2548.5	39227		2	2523.7	39612
	2	2547.7	39239		3	2522.7	39628
	1	2546.8	39253		2	2522.1	39638
	4	2545.6	39272	2521.6	2	2521.6	39645
2545.0	6	2544.9	39283		1	2520.9	39656

Table I (cont'd.)

Cameron & Elliott	Present experiments			Cameron & Elliott	Present experiments		
λair	I	λair	νvac	λair	I	λair	νvac
	2	2520.0	39671	2499.2	3	2499.9	39990
	4	2519.0	39686		2	2499.0	40004
	4	2518.3	39697		3	2498.0	40020
	2	2517.2	39715		0	2496.8	40039
	1	2516.5	39726		3	2496.0	40052
	4	2515.3	39745		2	2495.4	40062
	5	2514.5	39757		2	2495.2	40065
	2	2513.6	39772		2	2494.5	40076
					2	2492.7	40105
2513.5	3	2513.2	39778	2491.7	1	2491.8	40119
	3	2512.2	39794				
	4	2511.4	39806		1	2491.3	40128
	2	2510.6	39819		2	2490.9	40134
	1	2509.7	39833		2	2490.3	40144
	1	2509.3	39840		4	2489.6	40155
	2	2508.8	39848		2	2489.1	40163
	2	2508.1	39859		2	2487.0	40197
	1	2507.7	39865		2	2486.6	40203
	1	2507.3	39872	2485.4	1	2485.6	40220
	1	2506.7	39881		1	2484.0	40246
2506.4	3	2506.0	39892		0	2483.3	40257
	3	2505.2	39905		1	2481.3	40289
	4	2504.7	39913		1	2480.7	40299
	2	2504.2	39921		3	2480.1	40309
	4	2503.3	39936		1	2478.5	40335
	1	2501.7	39961	2477.2	3	2477.2	40356
	1	2500.7	39977		2	2476.9	40361

Table I (cont'd.)

Cameron & Elliott	Present experiments		Cameron & Elliott	Present experiments		
λair	I	λair	νvac	λair	I	λair	νvac
	1	2476.4	40369		0	2448.5	40829
	4	2475.7	40380	2448.1	2	2448.0	40837
	4	2474.6	40398		2	2447.6	40844
	1	2472.4	40434		1	2446.8	40857
	3	2472.0	40441		2	2445.2	40887
	1	2471.3	40452		2	2443.6	40911
2470.0	1	2470.1	40472		2	2440.8	40957
	2	2469.5	40482		1	2439.1	40986
	2	2469.1	40488		3	2437.5	41013
	3	2468.7	40495	2434.3	3	2433.9	41074
	2	2466.9	40525		1	2433.7	41077
	2	2466.3	40535		2	2432.6	41096
	1	2465.9	40541		2	2431.6	41113
	4	2464.5	40564	2427.9	2	2426.8	41194
	3	2463.0	40589	2420.7	1	2420.1	41308
2462.2	3	2462.3	40600		2	2418.8	41330
	3	2461.9	40607		1	2417.4	41354
	2	2460.9	40623		1	2415.7	41383
	2	2459.9	40640		1	2413.5	41421
	1	2458.1	40670	~~2405.9~~	1	2410.3	41476
	2	2457.6	40678	2405.9	2	2405.2	41564
	1	2457.0	40688		1	2404.5	41576
	1	2455.3	40716		2	2403.9	41586
	2	2454.9	40723		1	2402.4	41612
	1	2454.5	40729		2	2400.3	41649
	2	2452.2	40767	2392.8	1	2391.3	41805
					1	2390.9	41813
					1	2390.4	41821

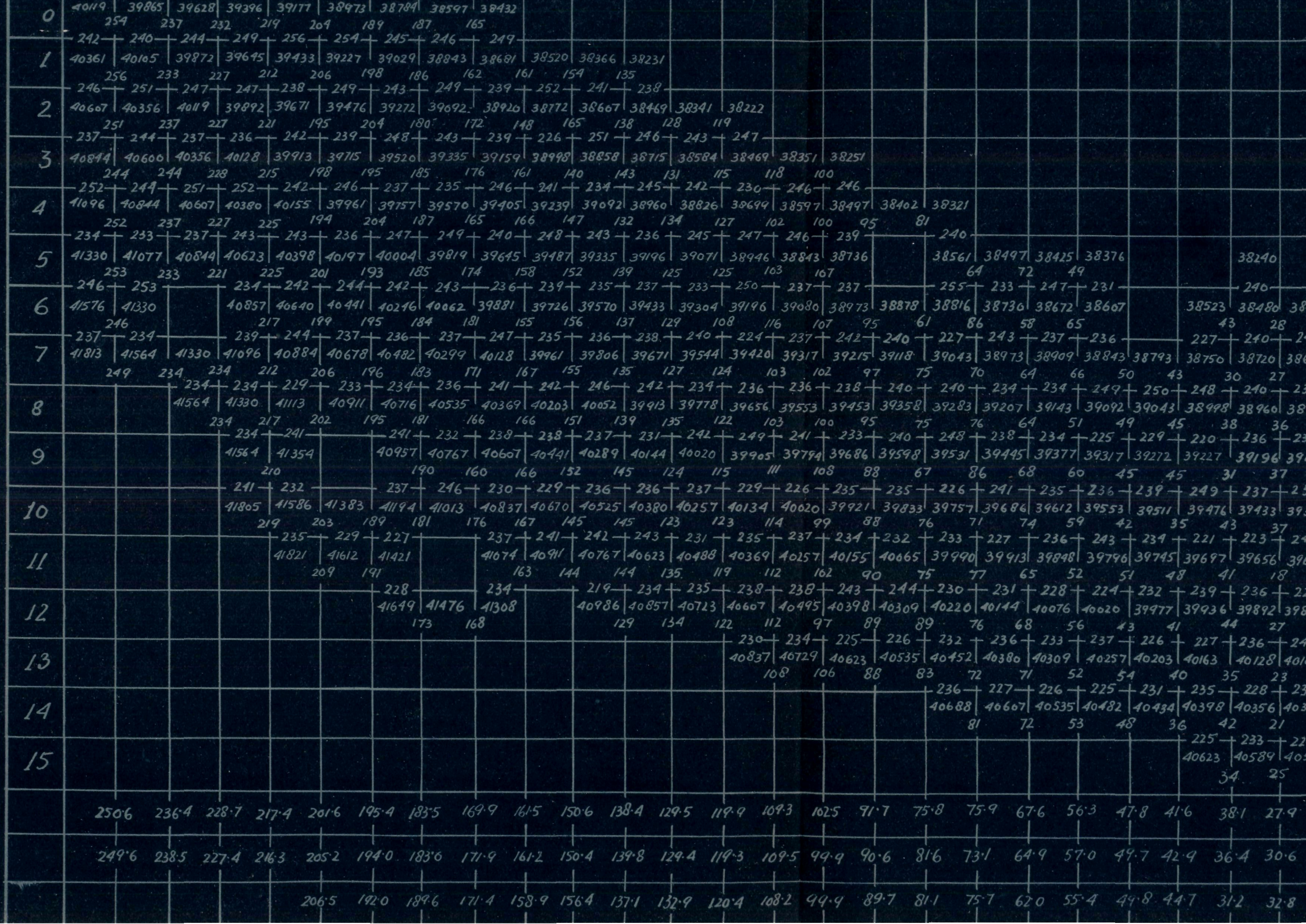
region 2600-2390 A is given in table II and the corresponding Frank-Condon parabola in table III. As can be seen from table II, the $\triangle G(v + \frac{1}{2})$ values obtained for the lower state of this system are in good agreement with those obtained by Elliott[15] for the upper state of the visible absorption bands of chloride. All the bands could be fairly well represented by the formula

$$\nu = 40115 + (246.6v' - 0.615\ v'^2) - (255.2\ v'' - 5.5\ v''^2 - 0.0155\ v''^3 + 0.00115\ v''^4)$$

The $\triangle G(v + 1/2)$ values calculated from the vibrational constants of this formula are included in table II to facilitate comparison with the corresponding observed values. The lower state of the system is very likely the $^3\Pi\ (O_u^+)$ state at 17658 cm^{-1} established by Elliott[15] from which the position of the upper state comes out to be 57783 cm^{-1}.

Isotopic Shifts.

There are three isotopic species $Cl^{35}\ Cl^{35}$, $Cl^{35}\ Cl^{37}$ and $Cl^{37}\ Cl^{37}$ for the chlorine molecule with the natural abundance ratio of 9.9 : 6.3 : 1. The bands corresponding to $Cl^{37}\ Cl^{37}$ are supposed to be extremely weak to be observable with any certainty. It is expected that the bands corresponding to $Cl^{35}\ Cl^{35}$ will be accompanied by bands corresponding to $Cl^{35}\ Cl^{37}$ with a corresponding intensity ratio of 1.57 : 1. If one assumes that the vibrational analysis shown in table II corresponds to $Cl^{35}\ Cl^{35}$ molecule, about 46 bands can be



v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
0	1	1	3	3	3	7	0	1	0																	
1	2	2	1	2	1	4	3	2	4	2	1	1														
2	3	3	1	3	2	2	4	8	10	5	4	2	1	1												
3	2	3	3	1	4	2	1	2	3	4	4	2	1	2	1	1										
4	2	2	3	4	4	1	4	4	1	2	8	3	4	0	1	0	2	0								
5	2	1	2	2	4	2	2	2	2	2	2	6	4	2	2	5		1	0	1	2			1		
6	1	2		1	2	3	1	2	1	1	4	1	7	6	4	7	3	5	5	2	4		1	2	2	
7	1	2	2	2	2	2	2	1	1	1	4	2	4	3	2	1	2	6	7	1	2	2	1	4	1	
8			2	2	2	2	1	2	1	2	3	4	3	1	2	1	1	6	1	2	8	6	4	3	3	
9				2	1		2	2	3	3	1	2	3	3	3	4	1	3	4	2	2	4	4	6	3	
10				1	2	1	2	3	2	1	2	4	0	2	3	2	1	4	4	2	1	1	2	1	3	
11					1	1	1		3	2	2	2	2	1	0	4	2	3	4	2	3	4	4	1	2	2
12							2	1	1		1	1	2	3	3	4	3	1	2	2	3	1	4	3	1	1
13														2	1	2	2	1	4	3	0	2	2	1	2	2
14																		1	3	2	2	1	4	3	1	3
15																							2	3	4	1

TABLE III.

accounted to have isotopic components corresponding to Cl^{35} Cl^{37}. Table IV shows the observed and calculated values for the probable isotopic displacements. All the isotopic components can also be fitted well in the vibrational scheme of Cl^{35} Cl^{35} with different (v', v") values and are also shown as such in table II. It is probably because of such overlapping that the relative expected intensity variation of 1.57 : 1 is not maintained in table IV and therefore the identification of the isotopic displacements can not be said to be completely unambiguous.

The Electronic Transition Involved.

The lower state of this system is the $^3\Pi\ (O_u^+)$ state with the electronic configuration $\sigma_g^2\,\pi_u^4\,\pi_g^3\,\sigma_u$. It is difficult to say with certainty which electronic term is actually involved for the upper state unless the rotational structure of the band system is worked out. The plates taken with the 1st and 2nd orders of a 21-ft grating spectrograph in the present experiments do not reveal the necessary rotational structure.

However, following the term scheme developed by Mulliken[16] for iodine molecule and extended by Asundi and Venkateswarlu[17] for bromine and chlorine molecules, one can see that the configuration that gives stable "gerade" states around 50,000 cm^{-1} to 60,000 cm^{-1} is $\sigma_g^2\,\pi_u^2\,\pi_g^4\,\sigma_u^2$ which gives the electronic states $^3\Sigma_g^-\ (O_g^+ / g)$, $^1\Sigma_g^+\ (0_g^+)$ and $^1\Delta_g\ (2_g)$. Of these, the last term is not expected to combine with

TABLE IV.

The Probable Isotopic Shifts for the Band System [illegible]00 - 2390A.

v', v"	ν in Cm-1	I	Δν Obs. Cm-1	Calc.
6 , 24	38440	0	12	12
	38452	2		
2 , 11	38469	2	11	13
	38480	2		
6 , 23	38469	2	11	10
	38480	2		
3 , 12	38584	1	13	11
	38597	1		
2 , 10	38607	4	14	12
	38621	1		
7 , 25	38655	1	17	16
	38672	2		
1 , 8	38681	4	18	14
	38699	0		
2 , 9	38772	5	12	12
	38784	0		
7 , 21	38784	0	9	11
	38793	2		
3 , 10	38858	4	8	9
	38866	3		
8 , 23	38946	2	14	17
	38960	3		
8 , 21	39029	3	14	14
	39043	6		
8 , 20	39080	4	12	13
	39092	8		
9 , 23	39177	3	19	20
	39196	6		
1 , 5	39227	4	12	10
	39239	2		
9 , 22	39207	1	20	18
	39227	4		

Table IV (cont.)

v' , v"	in Cm^{-1}	I	Obs. $\Delta\nu$ Cm^{-1}	Cal. $\Delta\nu$ Cm^{-1}
9 , 21	39253 39272	1 4	19	17
0 , 3	39396 39405	3 1	9	9
9 , 18	39433 39445	1 4	12	13
9 , 16	39591 39598	1 1	7	11
10 , 19	39598 39612	1 2	14	17
0 , 2	39628 39638	3 2	10	6
11 , 24	39612 39638	2 2	26	27
10 , 18	39671 39686	2 4	15	16
11 , 22	39671 39697	2 4	26	24
11 , 21	39726 39745	1 4	19	23
11 , 20	39772 39794	2 3	22	22
11 , 19	39833 39848	1 2	15	20
12 , 24	39833 39865	1 1	32	30
12 , 23	39859 39892	2 3	33	29
9 , 13	39892 39905	3 3	13	9
8 , 11	39905 39913	3 4	8	6
11 , 18	39892 39913	3 4	21	19
11 , 17	39977 39990	1 3	13	18

Table IV (cont.)

v' , v"	$\tilde{\nu}$ Cm^{-1}	I	$\Delta\tilde{\nu}$ obs. Cm^{-1}	$\Delta\tilde{\nu}$ Cal. Cm^{-1}
10 , 14	40004	2	16	12
	40020	3		
13 , 25	40039	0	37	35
	40076	2		
11 , 15	40144	2	11	16
	40155	4		
13 , 18	40356	3	24	25
	40380	4		
12 , 15	40380	4	18	19
	40398	4		
12 , 24	40472	1	23	18
	40495	3		
12 , 13	40589	3	18	18
	40607	3		
3 , 0	40829	0	15	11
	40844	2		
4 , 0	41077	1	19	14
	41096	2		
8 , 4	41096	2	17	16
	41113	2		
5 , 0	41308	1	22	18
	41330	2		
8 , 3	41308	1	22	17
	41330	2		

$^3\Pi(O_u^+)$ state with any appreciable intensity as the transition is prohibited for case C type coupling. Venkateswarlu and Verma attributed $^3\Sigma_g^-(O_g^+ \sigma/_g)$, $^1\Sigma_g^+(O_g^+)$ to the upper states of the band systems 3150 - 2970A and 2950- 2670A respectively in the bromine molecule. The present 2600-2390A system in chlorine appears to be analogous to the 2950-2670A system of bromine and therefore the $^1\Sigma_g^+(O_g^+)$ term can probably be attributed to the upper state of the system. Thus the probable transition in the emission of the present band system in chlorine may be written down as

$$\sigma_g^2 \pi_u^2 \pi_g^4 \sigma_u^2 \; ^1\Sigma_g^+(O_g^+) \rightarrow \sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u \; ^3\Pi(O_u^+)$$

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CHAPTER II.

Emission spectrum of chlorine excited in the presence of Argon.

Part II.

The Band system in the region 2365-2239A.

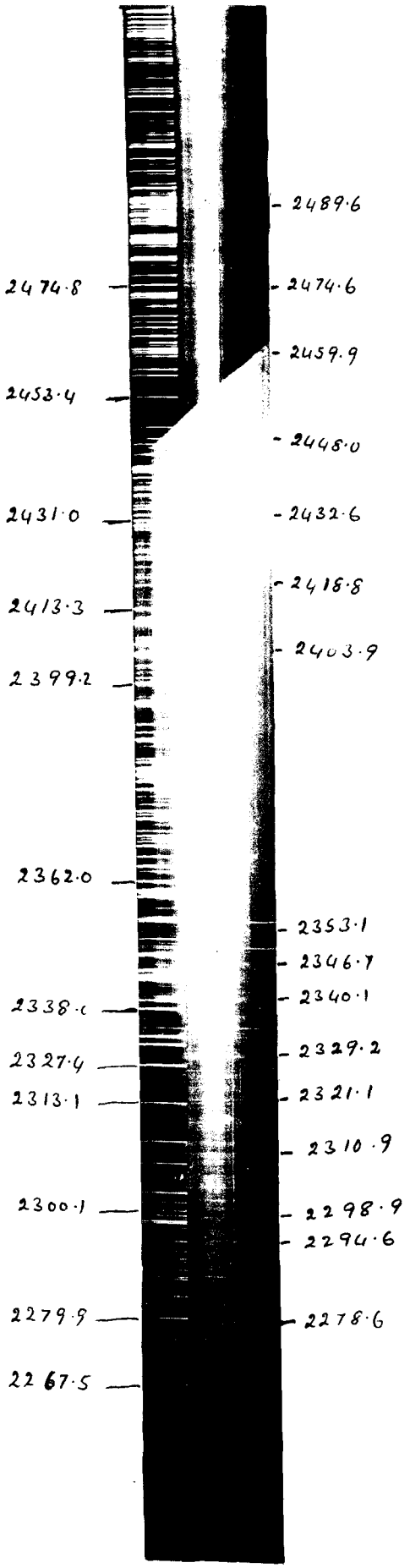

FIGURE I.

The enlargement of the 2365-2239A system of chlorine obtained in the first order of a 21-ft grating spectrograph.

Emission Spectrum of Chlorine Excited in The Presence of Argon.

Part II: The Band System in the Region 2365 - 2239A.

Abstract

The weak band system in the region 2365-2239A is discussed in this chapter. The wavelengths and the wavenumbers of the bands photographed with the first order of a 21-ft grating spectrograph are recorded. The vibrational analysis of the bands and their corresponding intensity distribution are also given. The analysis shows that the lower state of the system is the same as that of the 2600 - 2390A system discussed in the earlier chapter and is the $^3\Pi(0u^+)$, established by Elliott at 17658 cm^{-1}. The constants of the upper state are $\omega_e' = 261.5\ cm^{-1}$, $\omega_e x_e' = 0.812\ cm^{-1}$, $T_e = 61290\ Cm^{-1}$

Introduction.

Chlorine when excited in the presence of argon has been stated in the earlier chapter to give two band systems: (1) a strong and extensive system in the region 2600 - 2390A and (2) a weak system in the region 2365 - 2239A. The experimental data and the vibrational analysis of the band system in the region 2600 - 2390A is given in the earlier chapter. The present chapter deals with the band system in the region 2365 - 2239A.

Experimental Data and Vibrational Analysis.

Using the same experimental set up as described in the earlier chapter, the band system was recorded with a Hilger Medium Quartz Spectrograph as well as with a 21-ft grating spectrograph in the first order. The wavelengths and wavenumbers of the band heads are given in Table I along with their visually estimated relative intensities.

TABLE I.

Wavelengths, wavenumbers and relative intensities of the bands in the system 2365 - 2239A.

I	λair	νvac	I	λair	νvac
0	2364.6	42277	1	2343.7	42655
1	2363.5	42297	2	2343.3	42662
1	2362.1	42322	1	2343.1	42665
1	2361.7	42329	0	2342.2	42682
0	2360.9	42380	2	2341.3	42698
1	2358.2	42392	7	2340.1	42720
3	2357.5	42405	4	2339.8	42726
1	2357.1	42412	1	2339.4	42733
1	2356.4	42425	3	2338.3	42753
4	2353.1	42484	2	2337.8	42762
3	2352.5	42486	2	2337.3	42771
1	2352.0	42504	5	2336.7	42782
1	2351.4	42515	1	2336.3	42790
1	2351.0	42522	2	2335.1	42812
1	2350.7	42527	1	2334.0	42832
4	2350.3	42535	6	2332.8	42854
1	2349.7	42546	2	2331.2	42883
2	2349.1	42558	2	2330.4	42898
4	2346.7	42600	5	2329.7	42911
4	2346.0	42613	9	2329.2	42920
3	2345.1	42629	8	2328.9	42926
1	2343.3	42643	6	2326.5	42970
4	2343.9	42651	2	2325.7	42985

Table I (cont.)

I	λair	νvac	I	λair	νvac
2	2325.3	42992	4	2302.1	43425
5	2324.4	43009	4	2301.4	43438
4	2323.3	43029	10	2298.9	43486
4	2322.8	43038	4	2297.4	43514
1	2321.6	43061	4	2296.5	43531
6	2321.1	43070	3	2296.0	43541
2	2320.9	43074	8	2294.6	43567
5	2320.3	43085	1	2293.6	43586
3	2319.4	43101	1	2292.1	43615
4	2317.5	43137	2	2291.2	43632
4	2316.7	43152	0	2290.4	43647
2	2315.9	43167	2	2289.7	43660
4	2315.4	43176	3	2289.1	43672
3	2314.9	43185	0	2288.6	43681
2	2314.1	43200	3	2287.8	43696
0	2312.5	43230	6	2286.7	43718
7	2310.9	43260	6	2285.9	43733
6	2310.3	43271	2	2285.4	43743
2	2310.0	43276	4	2284.2	43765
5	2309.6	43284	2	2283.5	43779
1	2307.8	43318	2	2282.5	43798
6	2306.8	43337	2	2281.3	43821
2	2306.2	43348	3	2278.6	43873
8	2304.4	43382	2	2278.0	43885
4	2303.7	43395	5	2276.9	43906
4	2303.0	43408	1	2276.0	43923

Table I (cont.)

I	λair	ν̃vac
4	2272.6	43939
3	2271.8	44004
3	2270.9	44022
1	2270.1	44037
0	2269.4	44051
0	2268.2	44074
4	2267.6	44086
0	2266.0	44117
1	2265.2	44133
1	2263.1	44174
0	2261.6	44203
1	2260.4	44226
0	2257.1	44291
1	2256.2	44309
0	2253.6	44360
1	2252.5	44381
2	2252.2	44387
2	2251.3	44405
1	2247.7	44476
2	2240.0	44629
2	2239.2	44651

The band heads in general appear tobe degraded towards shorter wavelengths, though there are a number of bands for which the degradation is not certain. As the bands are quite weak, the error in the measurements of the positions of band heads may be estimated to be ± 3 cm^{-1}.

The vibrational scheme of the band system and the corresponding intensity distribution are given in Tables II and III. The $\Delta G''(v + 1/2)$ values obtained for 2600 - 2390A system discussed in the earlier chapter. All the bands could be fairly well represented by the formula

$$\nu = 43632 + (261.5v' - 0.812v'^2) - (255.2v'' - 5.5v''^2 - 0.0155v''^3 + 0.00115v''^4)$$

The constants used for the lower state of this system are the same as those used for the lower state of the 2600 - 2390A band system, which in turn are fairly close to those obtained by Elliott[3] for the $^3\pi(0_u^+)$ state at 17658 cm^{-1} from the vibrational analysis of the visible absorption bands of chlorine. [It appears that it would be useful to clarify the confusion that has probably led to the listing of different vibrational constants for the $^3\pi(0_u^+)$ state in the literature by different people. Elliott[1] in his first paper on the absorption spectrum of chlorine gave the rotational analysis for three bands having origins at 19258 cm^{-1}, 19389 cm^{-1} and 19509 cm^{-1} and analysed them as having (v'' , v') values as (2 , 17),

The Vibrational scheme of the band system 2365-2239A. of ~~Cl~~ Cl_2

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
0	2	8	4	5	2	3	1																				
1	2		4	4		3	2	0																			
2		5	2	4		5	2	3																			
3	2	1	1	3		6	2	2	7	2	3																
4			1		6	4	6	4	6	2	2	1	1	0													
5				0	4	2	1	4		6	9	5	4	4	1	1											
6						1		2	10	1	4	4		5	0		4		1								
7							4	5	6		4	5	4	4	8	1	1	4		1							
8								1		2	3	4	4	5	4	2	2	2	1	2		1	4		1		
9									1	0	1	2	0	4	4	1	0		5	5		2	6		1	2	
10									1	1	1	3		2	2	8		4			2		3	6	4	5	2
11														3	5			2	8				2	1	5	7	
12											2		1			0		3		2	0	2	1				
13															2	0	0	0			1	3		2	4		6
14															2			0									

TABLE III.

Intensity distribution and Franck-Condon Parabola for the bands in the system 2365-2239A. of Cl_2

(2 , 18) and (2, 19) respectively. He measured also the rotational isotopic shift for the second of these bands and gave 19379.4 cm^{-1} as the origin of the isotopic band. Birge[2] in his paper presented at the American Physical Society meeting on Dec 7th. 1929, stated that to explain isotopic effect it was necessary to decrease Elliott's v' numbering by 2 units. Later Elliott[3] did further experimental work and obtained the rotational constants of four more bands attributed to Cl^{35} Cl^{35} with band origins at 17890.9 ~~17809.9~~ cm^{-1}, 18076.1 cm^{-1}, 18250.4 cm^{-1} and 18840.2 cm^{-1}. He analysed also the rotational structure of two weak bands which have origins at 17892.5 cm^{-1} and 18837.6 cm^{-1} and which have been attributed to the Cl^{35} ~~35~~ Cl^{37} ~~37~~ molecule. Elliott states in his second paper that Birge had shown from his (Elliott's) new data that the bands originally designated as (2,17), (2, 18) and (2, 19) have to be redesignated as (1, 11), (1, 12) and (1, 13). Adopting this change, Elliott assigned the transitions (2, 6), (2, 7), (2, 8) and (2, 12) to the bands having the origins at 17890.9 cm^{-1}, 18076.1 cm^{-1}, 18250.4 cm^{-1} and 18840.2 cm^{-1}. The weak bands with origins at 17892.5 cm^{-1} and 18837.6 cm^{-1} were attributed to the Cl^{35} ~~35~~ Cl^{37} ~~37~~ molecule with the transitions (2, 6) and (2, 12) respectively.

On this basis he gave the vibrational assignment of all the absorption bands and showed that the assignment was supported by the isotopic shifts observed. Birge's[2] talk at the American Physical Society meeting was based

only on the first published data of Elliott[1] and the correction was apparantly meant to be applied for the v' numbering of Elliott in his first paper. With his new data later obtained, Elliott in consultation with Birge decreased each v' numbering by 1/2 (not by 2 as originally suggested by Birge) and v" numbering by 6. No further change was necessary in his v',v" numbering. Weizel[4], however, applied Birge's original suggestion to Elliott's revised data and decreased the v' numbering by 2 units. The isotopic shifts calculated according to Weizel's analysis are given for comparison in Table IV along with that of Elliott's observed and calculated shifts. It is evident that Weizel's analysis is wrong which is because of the unnecessary correction he applied to the numbering given in Elliott's revised analysis. Herzberg[5], probably, did not take note of this fact while listing the constants given by Weizel in his (Herzberg's) book.

Assuming that the lower state of the system is $^3\Pi(O_u^+)$ established by Elliott at 17658 cm^{-1}, the position of the upper state comes out to be 61290 cm^{-1}.

Isotopic Shifts.

If one assumes that the vibrational analysis shown in Table II corresponds to Cl^{35} Cl^{37} molecule, abut 30 bands of that table can be accounted to have isotopic components corresponding to Cl^{35} Cl^{37}. Table V shows the observed and calculated values for the

TABLE IV.

$Cl_{35}Cl_{35}$ $\nu_{obs.}$	$Cl_{35}Cl_{37}$ $\nu_{obs.}$	$\Delta\nu$ observed	Elliott's assingment	$\Delta\nu$ (calculated) from Elliott's assignment	Weizel's assignment.	$\Delta\nu$ (calculated) from Weizel's assignment.
			v" v'		v" v'	
19389.0	19379.4	+9.6	1 , 12	+10.1	1, 10	+5.4
17890.9	17892.5	-1.6	2 , 6	-1.6	2 , 4	-6.8
18840.2	18837.6	+2.6	2 , 12	+2.9	2 ,10	-0.5

TABLE V.

The probable vibrational levels for the band system 3365-3391 Å

v', v''	ν in cm^{-1}	I	$\Delta\nu$ obs. in cm^{-1}	$\Delta\nu$ calc. in cm^{-1}
6 , 13	42934 42939	1 1	7	5
[illegible] , 10	42405 42419	[illegible] 1	7	8
0 , 5	42495 42509	3 1	9	14
7 , 12	42954 42515	1 1	11	9
[illegible] , 11	42522 42527	[illegible] 1	5	5
[illegible] , 22	42600 42613	4 4	13	16
2 , 7	42629 42643	2 1	14	9
7 , 17	42643 42651	1 4	[illegible]	7
4 , 10	42662 42667	2 1	[illegible]	5
3 , 8	42720 42726	7 4	6	7
1 , [illegible]	42752 42763	3 2	[illegible]	9
[illegible] , 17	42822 42837	2 2	15	10
[illegible] , 21	42852 42867	2 [illegible]	15	13
[illegible] , 19	42918 42939	2 5	17	16
[illegible] , 15	43061 43071	1 [illegible]	13	[illegible]

Table V (cont'd.)

v', v''	ν cm^{-1}	T	obs. $\Delta\nu$ cm^{-1}	cal. $\Delta\nu$ cm^{-1}
9 , 15	43070 43085	6 5	15	14
10, 22	43071 43101	5 3	27	23
9 , 14	43107 43176	2 4	2	3
1 , 3	43176 43185	4 3	9	5
8 , 13	43276 43284	2 5	8	7
11, 21	43310 43340	1 2	30	26
9 , 13	43511 43531	4 4	17	11
11, 18	43541 43567	3 3	26	21
11, 17	43615 43632	1 2	17	19
9 , 10	43660 43672	2 3	12	8
11, 14	43705 43706	2 5	21	17
11, 13	44004 44022	3 3	13	17
10, 9	44291 44309	0 1	13	15
8 , 0	44387 44405	2 2	13	12
12, 10	44629 44651	2 2	22	20

probable isotopic displacements. All the isotopic components can also be fitted well in the vibrational scheme of Cl^{35} Cl^{35} molecule with different (v', v") values and are also shown as such in Table II. As in the case of the band system 2600 - 2390A discussed in the earlier chapter, it is again because of such overlapping that the identification of the isotopic band heads can not be said to be unambiguous.

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CHAPTER III.

Emission spectrum of Bismuth Monochloride.

Part I.

Vibrational analysis of the 6170 - 4220A system.

Emission Spectrum of Bismuth Monochloride.

Part I: Vibrational Analysis of the 6170 - 4220 A System

Abstract.

Bismuth chloride has been excited in a running condition with an uncondensed transformer discharge. About 390 bands are observed in the present experiments of which only 140 were recorded by earlier workers either in absorption or in flame spectra. The vibrational constants obtained are the same as those obtained by Morgan from absorption experiments except for the addition of a cubic term for the upper state. It appears quite likely that the upper state of the system dissociates into $Bi(^4S_{3/2}) + Cl(^2P_{3/2})$ atoms while the lower state, which is probably the ground state dissociates into $Bi(^4S_{3/2}) + Cl(^2P_{3/2})$. The rough values of the Dissociation energies obtained by extrapolations are $D_o' = 3750\ Cm^{-1}$ and $D_o'' = 24614\ Cm^{-1}$.

Introduction.

Visible bands in the region 4300 - 5400A attributed to bismuth monochloride are well known from a long-time back. Saper[1] excited the vapour of bismuth trichloride in active nitrogen and analysed the bands in the region 4300 - 5400A as emitted by the diatomic bismuth monochloride molecule. His analysis was confirmed by the observed isotopic shifts which tallied fairly well with those calculated from the BiCl molecule. Ghosh[2], however, rephotographed the bands lying in the region 4300 - 6600A by feeding the carbon arc with metallic bismuth or bismuth trichloride and attributed them to the BiO molecule. Morgan[3] studied bismuth halides extensively by taking the absorption spectrum of all of them. Halogens were passed over

molten mass of bismuth which was placed inside the furnace heated upto 900 - 1400°C. He obtained all the systems also, by placing the halides also inside the furnace. Two systems one in the region 5400 - 4300A and the other lying in the region 4000 - 3600A were obtained in the Bismuth monochloride molecule. He noticed the isotopic shifts of the right magnitude for the band heads of BiCl and BiBr molecules. The presence of isotopic shifts in addition to the presence of analogous systems in all the halides led him to conclude that these bands are due to bismuth halides.

Ray[4] further studied the spectrum of bismuth monochloride in absorption and also in emission by feeding the carbon arc with bismuth trichloride. He confirmed the formula proposed by Morgan[3] for the less refrangible system and showed that the emitter of the system is BiCl molecule.

However, in the experiments of all the workers above mentioned there was a possibility of the presence of different impurities as the experiments were conducted in the open atmosphere. Therefore, it was felt necessary to obtain these bands using a discharge tube avoiding the presence of atmospheric gases and thus to give a much more experimental proof for them. As no rotational structure was observed and analysed so far for this molecule, it was expected that such a work will help us to determine the rotational constants and the electronic transitions involved. Further it was also expected that the transformer discharge might give larger number of new bands which might help us to extend

and improve the vibrational analysis.

The experiments performed were found to be quite successful to develop the system 6170 - 4220A extensively. The present chapter deals with the vibrational analysis of the bands so developed and the rotational analysis is discussed in the next chapter.

Experimental Details.

The discharge tube, having cylinderical nickel electrodes placed coaxially along the length of the discharge tube, was 40 cms in length and 0.8 cms in diameter. The discharge tube was continuously pumped out from one end of it through a stop-cock whereas at the other end of it a side tube containing bismuth trichloride was attached. Since $BiCl_3$ is hygroscopic, it was dehydrated completely before starting the experiment.

The vapour was excited by an uncondensed transformer discharge applying 15 K.V. with a Hilger 1/4 K.w. power transformer. The discharge tube near the electrodes as well as the side tubes containing the sample were heated continuously by a Bunsen burner so as to maintain a sufficiently high pressure of the vapour. The sample obtained from two different sources i.e. B.D.H. and E.Merck was tried. The colour of the discharge was intense greenish blue. The less refrangible system in the region 6170 - 4220A was obtained. The other system lying on the shorter wavelength side of this system, (reported by previous workers) was

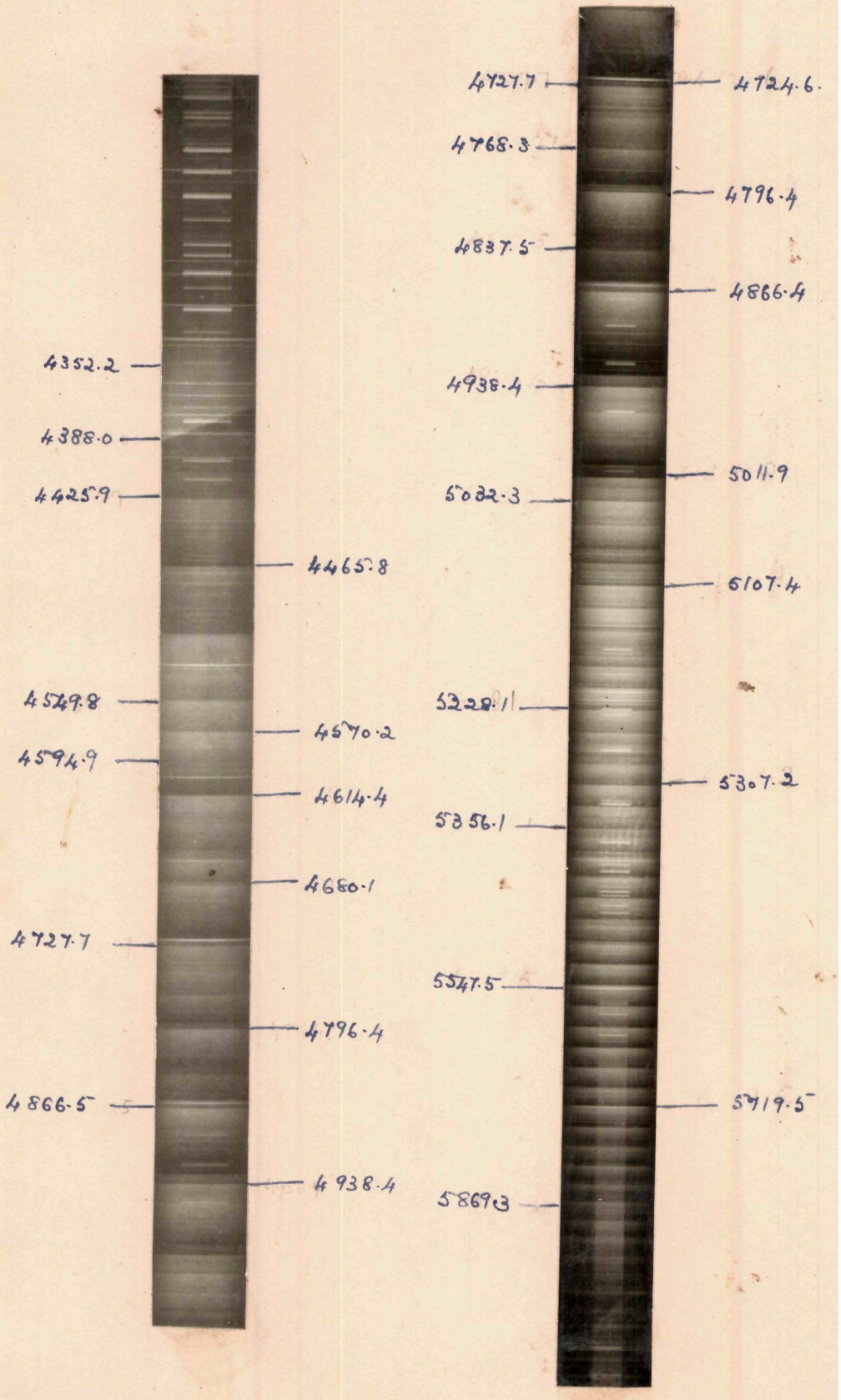
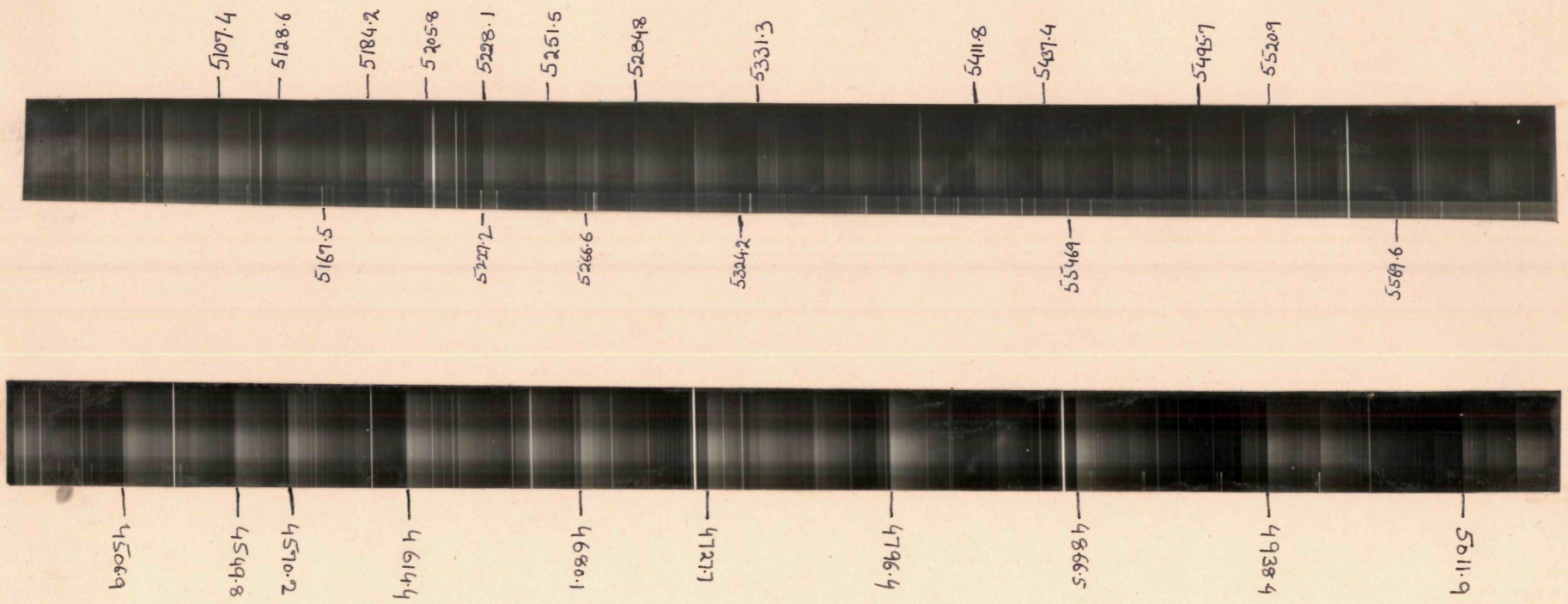


FIGURE I(A).

The enlargement of the 6170-4220A system of BiCl taken on a three prism glass spectrograph.

FIGURE I(B).

The enlargement of the 6170-4220A system of BiCl obtained on the first order of a 21-ft grating spectrograph.



not excited in the present experiments.

The spectrum was first taken on a three prism glass Zeiss Spectrograph having a dispersion of 11.4A°/m.m. at 4800A° and then on the first and second orders of a 21-ft grating spectrograph (Eagle mounting) with a dispersion of 2.5A°/m.m. and 1.25A°/m.m. respectively. The spectrum obtained from the three prism glass spectrograph was found suitable for vibrational analysis. Spectrogram taken on the three prism glass spectrograph along with that taken on the first order of a 21-ft grating spectrograph are shown in Fig. I. One to two hours exposures were needed to record the spectrum on the three prism glass spectrograph, whereas six hours were needed in the case of the 21-ft grating spectrograph. Measurements of the plates taken were carried out with a Zeiss Abbe Comparator.

Vibrational Analysis.

Wavelengths, wavenumbers and their visually estimated relative intensities are given in Table I. The bands observed by Morgan in absorption and by Rayin emission are also included in the table for comparison. It can be seen from the table that a large number of new bands have been recorded in the present experiments. The error involved in the present measurements may be $\pm$ 2 cm^{-1}. The agreement, between the measurements of all the bands observed in absorption and emission by previous workers and those measured in the present experiment, shows clearly that

TABLE I.

Wavelengths, Wavenumbers and Relative Intensities of the band System 6170 - 4220A.

~~Present Experiments~~ (Electrical excitation)

Morgan's ν vac	Ray's ν vac	Present Experiments λair	I	νvac	Morgan's νvac	Ray's νvac	Present Experiments λair	I	νvac
		6173.4	2	16194			5958.9	1	16777
		6145.7	0	16267			55.7	1	16786
		6093.6	2	16406			49.3	1	16804
		6088.4	2	16420			43.0	1	16822
		79.2	2	16445			38.4	1	16835
		69.2	1	16472			35.2	1	16844
		65.9	1	16481			30.6	3	16857
		57.8	1	16503			25.0	1	16873
		51.6	0	16520			20.1	1	16887
		45.7	1	16536			15.9	1	16899
		30.8	2	16577			08.9	3	16919
		27.1	1	16587			5901.6	5	16940
		10.5	0	16633			5893.2	1	16964
		02.2	2	16656			83.1	2	16993
		5997.5	1	16669			76.2	0	17013
		94.3	3	16678			71.4	2	17027
		89.2	1	16692			69.3	4	17033
		73.5	2	16736			64.5	2	17047
		69.6	2	16747			55.6	1	17073
		67.4	2	16753			49.4	1	17091
		63.2	3	16765			46.0	2	17101
							43.3	2	17109

Table I (continued)

Morgan's ν vac	Ray's ν vac	Present Experiments λ air	I	ν vac	Morgan's ν vac	Ray's ν vac	Present Experiments λ air	I	ν vac
		5839.8	4	17119			5702.6	1	17531
		35.1	2	17133			5697.4	2	17547
		30.6	1	17146			95.4	3	17553
		26.6	0	17158			90.6	5	17568
		21.5	1	17173			89.0	3	17573
		12.7	4	17199			69.3	2	17634
		11.3	6	17203		17601	61.6	5	17658
		05.3	2	17221			55.2	2	17678
		5799.3	2	17237			48.8	1	17698
		95.5	1	17250			37.6	0	17733
		91.1	1	17263		17749	33.2	6	17747
		84.8	1	17282			24.0	0	17776
		79.1	4	17299			20.5	0	17787
		75.1	2	17311		17835	04.8	6	17837
		66.4	1	17337			5599.7	1	17856
		59.8	1	17357		17916	80.7	0	17914
		55.1	1	17371		17935	75.4	6	17931
		50.2	4	17386			72.9	0	17939
		46.9	1	17396			57.1	0	17990
		41.9	2	17411		18025	47.5	5	18021
		5737.0	2	17426			36.8	0	18056
		32.0	1	17441			32.5	1	18070
		23.8	1	17466			27.6	1	18086
		19.5	5	17479			23.9	2	18098
		08.1	1	17514		18111	20.9	6	18108

Table I (continued)

Morgan's ν vac	Ray's ν vac	Present Experiments λ air	I	ν vac	Morgan's ν vac	Ray's ν vac	Present Experiments λ air	I	ν vac
		5512.7	2	18135	18837	18837	5307.2	5	18837
		01.1	1	18173		18858	03.0	2	18852
	18194	5495.7	4	18191		18904	5289.3	2	18901
	18209	5491.8	2	18204	18917	18917	84.3	4	18917
		87.9	0	18217	18947	18949	76.7	2	18946
	18273	71.6	4	18271		18982	66.4	1	18983
		68.0	0	18283	18994	18994	63.3	2	18994
	18300	63.9	5	18297	19037	19038	51.5	4	19037
		55.8	0	18324			46.0	0	19057
	18351	50.2	2	18343			34.1	1	19100
		43.9	2	18364	19124	19123	28.1	5	19122
	18388	37.4	6	18386		19182	5212.3	1	19180
		26.5	0	18423	19204	19204	05.8	3	19204
	18473	11.8	4	18473			5198.0	2	19233
18552	18553	5389.0	3	18551	19262	19264	90.7	2	19260
	18578	83.0	0	18572	19284	19284	84.2	4	19284
		69.1	1	18620	19322	19323	74.8	3	19319
	18633	65.6	2	18632		19339	69.2	1	19340
		61.6	0	18646	19360	19359	64.1	2	19359
	18668	56.1	4	18665			59.9	2	19375
	19703	45.0	3	18704	19410	19410	50.5	4	19410
		35.8	2	18736			48.7	1	19417
18754	18754	31.3	4	18752		19465	36.5	0	19463
		26.5	1	18769	19494	19494	28.6	6	19493
	18822	12.6	1	18818			24.2	2	19510

Table I (cntinued)

Morgan's ν vac	Ray's ν vac	Present Experiments λ air	I	ν vac	Morgan's ν vac	Ray's ν vac	Present Experiments λ air	I	ν vac
	19519	5120.7	0	19523		20076	4979.7	1	20076
19548	19547	15.0	4	19545	20095	20096	76.7	2	20088
19575	19574	07.4	8	19574			70.8	1	20112
	19610	5098.2	1	10609		20117	69.5	0	20117
	19627	94.6	2	19623			66.6	1	20129
		91.3	2	19636		20137	62.1	0	20147
19654	19652	87.1	4	19652	20164	20163	58.7	4	20161
	19663						55.0	1	20176
19702	19702	74.7	1	19700	20191	20190	52.1	2	20188
		68.8	1	19723		20200	49.4	1	20199
19785	19785	53.7	3	19782			46.4	0	20211
19805	19806	48.8	1	19801			42.5	1	20227
	19831	41.5	1	19830	20245	20244	38.4	10	20244
		36.9	0	19843	20281	20280	29.6	3	20280
19868	19867	32.3	7	19866	20284	20284	28.1	1	20286
		27.7	1	19884			21.1	0	20315
19898	19899	25.0	2	19895			11.7	0	20354
19911	19912	21.2	3	19910		20373	07.1	1	20373
		15.2	1	19934		20386	04.0	2	20382
19948	19948	5011.9	5	19947			02.8	0	20391
		08.4	1	19961			01.1	1	20398
19991	19991	01.6	3	19988		20404	4899.4	0	20405
		4998.1	0	20002		20419	97.2	1	20414
		91.9	1	20027			94.1	0	20427
		81.9	2	20067			91.5	0	20433

Table I (continued)

Morgan's ν vac	Ray's ν vac	Present Experiments λair.	I	ν vac	Morgan's ν vac	Ray's ν vac	Present Experiments λair	I	ν vac
	20460	4886.7	4	20458			4799.3	1	20874
	20484	81.2	1	20481		20878			
	20490					20899	94.5	0	20895
	20514	4873.1	0	20515			79.2	0	20910
20543	20543	66.5	3	20543			77.0	1	20919
		63.9	1	20554			74.0	1	20941
20572	20572	60.1	2	20570			71.0	0	20954
		59.4	2	20573	20970	20968	68.2	4	20966
20578	**20578**	**58.0**	**2**	**20579**					
		56.2	1	20586			63.2	2	20986
	20606	52.5	1	20602		20991			
		43.1	1	20642			55.4	2	21023
20670	20670	37.0	3	20669			49.7	1	21043
		35.4	1	20675	210 8	21051	47.5	5	21052
		33.3	0	20684	21075	21075	43.2	2	21074
	20696	31.2	1	20693			40.2	3	21091
		29.1	0	20702			36.2	1	21105
		27.0	1	20711			33.5	1	21118
		17.3	4	20750			28.6	1	21139
	20757	15.6	1	20760	21147	21146	27.2	1	21145
		12.8	1	20772			25.2	3	21154
	20781	10.7	1	20781	21158	21161	21.5	1	21169
		07.0	1	20797			21.2	1	21176
		03.3	1	20813			16.1	1	21199
20844	20843	4796.4	10	20843			12.2	1	21215
20866	20865	91.6	3	20864			10.6	1	21222

Table I (continued)

Present Experiments					Present Experiments				
ν	ν	λ	I	ν	ν	ν	λ	I	ν
		4709.0	1	21239			4631.4	0	21577
		07.0	1	21232	21578	21578	32.0	1	21573
		02.0	0	21256	21571	21577	30.6	1	21510
	21260	00.0	0	21267			31.0	0	21515
	21270	4697.4	1	21281			26.0	0	21529
		91.0	1	21283			20.0	0	21519
		79.6	1	21343	21561	21615	14.4	0	21615
21261	21261	6.1	7	21371	21570	21570	10.0	0	21578
21278	21278	77.7	0	21378			10.0	1	21616
		71.5	1	21310			01.5	0	21619
		70.0	1	21324			05.0	1	21702
		70.1	1	21327			02.1	0	21720
		67.7	0	21410	21751	21756	4594.0	0	21737
		61.7	1	21433		21777	99.7	0	21777
		64.0	0	21434			91.4	1	21795
1191	21810	49.0	1	21440			90.0	1	21814
21460	21460	4579.0	0	21462			91.4	0	21821
		37.0	1	21467			72.0	0	21839
21479	21479	53.7	0	21479			75.4	0	21843
		59.0	1	21491			74.1	0	21856
		47.7	1	21510			70.4	1	21874
		41.1	1	21521	21871	21875	70.4	0	21877
		40.0	0	21531			4561.0	0	21904
		40.4	1	21543			61.7	1	21931
		37.4	1	21547			57.0	1	21934

Table I (continued)

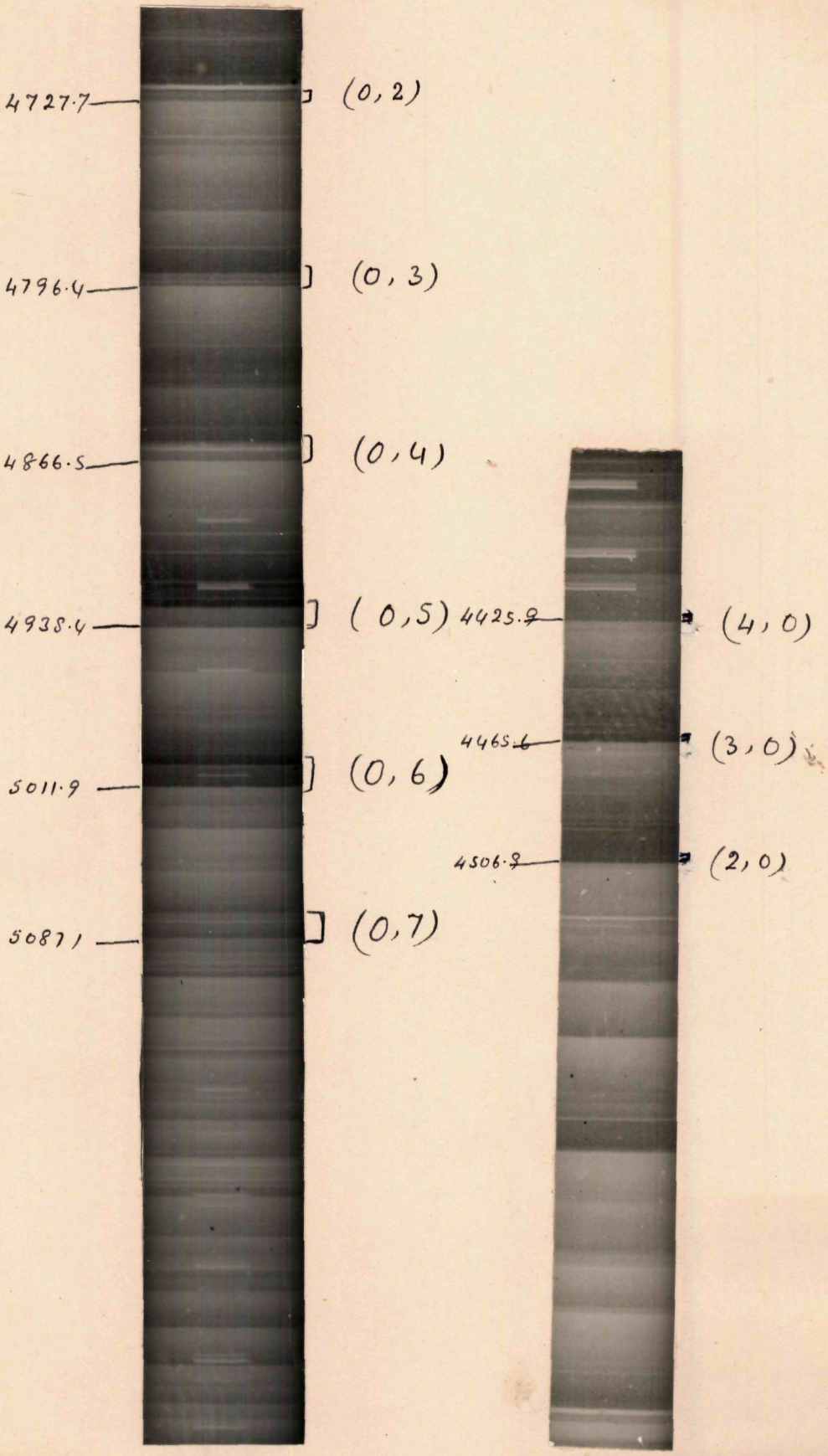
Present Experiments									
		4503.0	0	22196			4483.0	1	22296
21978	21978	[illegible]	[illegible]	21978			[illegible]	1	22295
		[illegible]	[illegible]	[illegible]			[illegible]	0	22311
		[illegible]	1	[illegible]			[illegible]	0	22351
		[illegible]	[illegible]	[illegible]		[illegible]	71.2	1	22359
		42.0	0	[illegible]	22374	22375	[illegible]	2	22374
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22387
		[illegible]	1	[illegible]			60.[illegible]	1	22411
		[illegible]	1	[illegible]		22427	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]			56.5	1	22439
	22061	[illegible]	[illegible]	[illegible]			54.5	0	22443
22071	[illegible]	[illegible]	[illegible]	[illegible]			53.1	0	22450
22078	22078	27.5	1	22081			51.5	0	22459
		[illegible]	1	[illegible]	22476	22477	47.7	3	22477
		[illegible]	1	[illegible]			36.5	1	22534
		[illegible]	1	[illegible]			34.7	3	22542
		[illegible]	1	[illegible]		22548	[illegible]	1	22575
		[illegible]	1	[illegible]	22578	22571	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	22580	22588	25.[illegible]	[illegible]	[illegible]
22177	22174	[illegible]	[illegible]	[illegible]			[illegible]	1	22598
22188	22188	[illegible]	[illegible]	[illegible]		22600	[illegible]	[illegible]	[illegible]
		4496.0	1	[illegible]			[illegible]	1	22613
	22645	[illegible]	[illegible]	[illegible]		22647	[illegible]	0	22647
		[illegible]	[illegible]	[illegible]		22650	13.[illegible]	1	22651
	22681	[illegible]	1	[illegible]			12.4	1	22657

Table I (continued)

Morgan's ν_{vac}	Day's ν_{vac}	Present λ_{air}	I	Present ν_{vac}	Morgan's ν_{vac}	Day's ν_{vac}	Present λ_{air}	I	Present ν_{vac}
22665	22667	4411.0	2	22664	23071		4334.2	0	23066
22707	22703	03.5	0	22703		23077	32.1	0	23077
22727	22726	4399.6	2	22723	23125	23130			
		96.7	0	22733	23159	23158	20.5 → 17.3	0 → 0	23139 → 23156
		95.0	0	22747			15.1	0	23168
		94.0	0	22752			11.6	0	23187
22760	22760	92.6	2	22759			10.6	0	23192
22783	22784	88.0	2	22783		23206	08.0	2	23206
		80.5	1	22822			4285.3	0	23329
22828	22834	78.6	~~2~~	22832			80.5	2	23355
22850	22854	75.3	2	22849			79.3	0	23362
		71.3	0	22870			60.5	0	23465
22882	22882	67.5	1	22890			57.8	0	23480
		66.3	0	22896			54.1	0	23500
22906	22904	64.2	1	22907	23513		51.8	2	23513
		59.7	0	22931			23.9	2	23668
		58.5	2	22937					
22946	22947	56.6	1	22947					
22971	22973	52.2	2	22970					
23006	23003	46.0	0	23003					
		42.3	0	23023					
23031	23034	40.8	1	23031					
		38.1	0	23045					
		36.8	1	23052					

FIGURE II.

Extra enlargement of some of the bands of the 6170-4220A system of BiCl showing the probable isotopic shifts.



the present system is the same as that observed by Morgan in absorption. Deslandres scheme for the band system in the region 6170 - 4220A is given in Table II and the corresponding intensity distribution in Table III. Table III corresponds to the more abundant molecule $BiCl^{35}$. All the bands could be fairly well represented within ± 4 cm^{-1} by the formula

$$\nu = 21757 + (217.8v' - 2.5v'^2 - 0.02v'^3) - (307.4v'' - 0.96v''^2)$$

in which the same constants are being used as reported by Morgan and Ray except that a negative cubic term has been added in the formula for the upper state.

Isotopic Shifts.

The abundance ratio of Cl^{37} and Cl^{35} being 1 : 3, we expect two isotopic band heads of BiCl molecule namely, $BiCl^{35}$ and $BiCl^{37}$ which will be having the intensity ratio of 3 : 1 respectively. The isotopic band heads for some of the strong bands are marked in fig II. For other strong bands, the isotppic heads are overlapped by the other bands and hence can not be shown clearly in the figure. The band heads which can be represented as isotopic components are listed in table IV, where the corresponding observed and calculated isotopic shifts are also included for comparison. Some of the bands which have been listed in Table IV as belonging to $BiCl^{37}$ can also be represented as belonging to $BiCl^{35}$ with different v', v" values and are, therefore, also shown as such in table II and IV.

TABLE III.

Intensity distribution and Franck-Condon Parabola for the bands in the system 6170-422A. of Biel

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
0	2	4	5	10	8	10	5	4	2									1																
1	5	6	7	5	1	4	4	7	8	4	2	3	0	2	1	3				1														
2	6	6	3	3	4	3	1	1	3	6	3	4	2	2	1	0		2	1															
3	6	1	2	3	1	1	2	3	3	1	4	5	5	3	4	0		1																
4	5	1	2	2	2	2	1	1	2	2	1	3	4	4	4	4	0	2	1	1	1													
5	2	3	3	2	2	3	4	1	2	2	1	2	2	2	4	6	6	6	3	1	0	2												
6	2	2	1	3	2	2	2	3	2						2	0	5	5	6	5	6	5	1											
7	0	2	2	2	1	0	1	1	4		1	1						2	6	5	4	4	3	1										
8	0	0	2	2	1	1	1	1	1	1	0	2								6	5	4	2	3	1									
9	0	0	1	5	1	1	0	1	1	1	0										0	1	4	5	3									
10		2	1	0	0	1	0	1			0	1	1							1		2	1	2	1	2								
11		2		1	1	0	0	0	1	1		1								0	0			1	2	2	1							
12		2	0	0	2	0	2	6		1		1	0										2	2	1	1	0							
13				2	1	2	0	1	0	0				1	0							1			4	4	1	0	0					
14						0	0	1	2	3	1				0									1	1	1	3	2	2					
15								1	2	1	0											2	2			2	2		1					
16						0		1	1	2	1	0														2	1		1	2				
17							1	1	2	0			2				1									2		2	1					
18							2	1	0		2	1	1	0															1					
19											6	2		2					2											2	1			
20							0		1	2	2	1		2															2					
21														1																		2	2	

TABLE IV.

The Probable Isotopic Shifts For the 6170 - 4220 Å System of BiCl.

v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$	v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
10, 25	16692 16577	1 2	115	114	8 , 21	17396 17299	1 4	97	99
14, 27	16777 16656	1 2	121	117	12, 23	17514 17411	1 2	103	100
16, 28	16736 16669	1 1	117	121	3 , 17	17531 17441	1 1	90	95
9 , 24	16736 16678	1 3	103	111	42, 22	17776 17678	0 2	98	95
11, 25	16844 16736	1 2	108	112	1 , 14	17939 17856	0 1	83	87
8 , 23	16873 16765	1 3	108	109	5 , 16	18191 18108	4 6	83	81
7 , 22	16964 16857	1 3	107	107	1 , 13	18217 18135	0 2	82	81
6 , 21	17040 16940	2 5	107	105	7 , 17	18283 18204	0 2	79	80
9 , 23	17047 16940	2 5	107	106	2 , 13	18423 18343	0 2	80	76
2 , 18	17073 16964	1 1	109	105	4 , 14	18551 18473	3 4	78	74
8 , 22	17133 17027	2 2	106	104	3 , 13	18620 18551	1 3	69	72
13, 25	17146 17033	1 4	113	109	6, 15	18646 18572	0 0	74	72
15, 26	17158 17047	0 2	111	112	5 , 14	18736 18665	2 4	71	70
7 , 21	17221 17119	2 4	102	102	1 , 11	18769 18704	1 3	65	69
12, 24	17250 17146	1 1	104	105	4 , 13	18818 18752	1 4	66	68
2 , 17	17337 17237	1 2	100	99	3 , 12	18901 18837	2 5	64	66

Table IV (continued)

v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$	v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
2 , 11	18933	1	66	64	0 , 6	19988	3	41	42
	18917	4				19947	5		
1 , 10	19057	0	63	63	3 , 8	20027	1	39	41
	18994	2				19988	3		
4 , 12	19100	1	63	62	2 , 7	20117	0	41	39
	19037	4				20076	1		
3 , 11	19180	1	58	60	5 , 9	20129	1	41	40
	19122	5				20088	2		
2 , 10	19260	2	56	58	1 , 6	20199	1	38	37
	19204	3				20161	4		
1 , 9	19340	0	56	56	7 , 10	20211	0	35	39
	19284	4				20176	1		
4, 11	19375	2	56	56	4 , 8	20227	1	39	37
	19319	3				20188	2		
0 , 8	19417	1	58	55	0 , 5	20280	3	36	35
	19359	2				20244	8to		
3, 10	19463	0	53	54	3 , 7	20315	0	35	35
	19410	4				20280	3		
2 , 9	19545	4	52	52	8 , 10	20391	0	37	36
	19493	6				20354	0		
1 , 8	19623	2	49	50	2 , 6	20405	0	32	33
	19574	6				20373	1		
0 , 7	19700	1	48	49	5 , 8	20414	1	32	33
	19652	4	48	49		20382	2		
2 , 8	19830	1	48	45	10, 11	20438	0	40	37
	19782	3				20398	1		
5 , 10	19848	0	47	46	4 , 7	20515	0	34	31
	19801	1				20481	0		
1 , 7	19910	3	44	44	0 , 4	20570	2	27	29
	19866	5				20543	6		
4 , 9	19934	1	39	43	11, 11	20586	1	32	35
	19895	2				20554	1		

Table IV (continued)

v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$	v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
6 , 8	20602	1	29	30	18 , 12	21230	1	32	36
	20573	2				21198	1		
3 , 9	20675	1	33	30	8 , 7	21239	1	16	17
	20642	1				21223	1		
2 , 5	20693	1	25	26	2 , 3	21281	1	14	12
	20668	3				21267	3		
5 , 7	20702	0	27	27	5 , 5	21281	1	14	14
	20675	1				21267	3		
7 , 8	20772	1	22	26	1 , 2	21372	2	11	10
	20750	4				21361	7		
1 , 4	20781	1	21	24	4 , 4	21382	1	10	11
	20760	1				21372	2		
4 , 6	20797	1	25	24	9 , 7	21407	1	13	14
	20772	1				21394	1		
0 , 3	20864	3	21	22	0 , 1	21458	2	9	8
	20843	8 10				21449	4		
3 , 5	20895	0	21	22	6 , 5	21467	2	9	10
	20874	1				21458	2		
3 , 8	20954	1	26	23	18 , 11	21510	1	26	26
	20928	1				21484	1		
2 , 4	20936	2	20	19	8 , 6	21531	0	10	10
	20966	4				21521	1		
5 , 6	20986	2	20	20	2 , 2	21580	1	8	6
	20966	4				21572	3		
1 , 3	21074	2	16	17	14 , 9	21593	0	21	18
	21058	5				21572	3		
4 , 5	21091	2	17	17	1 , 1	21672	2	7	3
	21074	2				21665	6		
11, 9	21154	0	21	22	15 , 9	21720	0	18	17
	21133	1				21702	1		
0 , 2	21160	2	14	15	20 , 11	21720	0	34	32
	21146	5				21686	1		

Table IV (continued)

v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
18, 10	21805	1	28	24
	21777	2		
8, 5	21821	0	5	4
	21816	1		
16, 9	21849	0	19	17
	21830	2		
12, 7	21884	2	9	8
	21875	6		
19, 10	21901	1	26	25
	21875	6		
15, 8	22009	0	9	11
	22000	2		
11, 6	22014	0	5	3
	22009	0		
13, 7	22029	1	9	7
	22020	1		
6, 3	22047	2	8	8
	22055	3		
3, 1	22077	0	4	6
	22081	1		
16, 8	22135	1	13	11
	22122	1		
5, 2	22163	2	10	7
	22173	3		
2, 0	22173	3	9	8
	22182	6		
7, 3	22232	1	11	7
	22243	2		
4, 1	22272	0	6	10
	22278	1		
9, 4	22278	1	8	6
	22286	1		
15, 7	22295	1	9	5
	22286	1		
6, 2	22351	0	8	10
	22359	1		
3, 0	22374	2	13	13
	22387	6		
10, 4	22443	0	7	8
	22450	0		
4, 0	22572	2	16	17
	22588	5		
9, 3	22572	2	16	13
	22588	5		
13, 5	22598	1	5	7
	22603	2		
6, 1	22647	0	17	17
	22664	2		
18, 7	22657	1	6	5
	22651	1		
8, 2	22703	0	20	17
	22723	2		
10, 3	22738	0	14	15
	22752	0		
14, 5	22738	0	9	8
	22747	0		
12, 4	22747	0	12	12
	22759	2		
5, 0	22759	2	24	21
	22733	2		
7, 1	22832	0	17	21
	22849	2		
9, 2	22870	0	20	19
	22890	1		
11, 3	22890	1	17	17
	22907	1		
13, 4	22896	0	11	13
	22907	1		

Table IV (continued)

v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
6 , 0	22947	1	23	24
	22970	2		
16, 5	22994	0	9	9
	23003	0		
10, 2	23031	1	21	22
	23052	1		
12 ,3	23045	0	21	19
	23066	0		
9 , 1	23168	0	24	26
	23192	0		
13, 3	23187	0	19	20
	23206	2		
10, 1	23329	0	26	29
	23355	2		
9 , 0	23465	0	35	33
	23500	0		
11, 1	23480	0	33	31
	23513	2		

The agreement between the observed and calculated isotopic shifts from the present experiments as well as that observed in absorption by Morgan and Ray indicate clearly that this band system can, most probably, be attributed to BiCl molecule.

The Dissociation Products and The Dissociation Energies of the States Involved.

The present band system occurs in absorption as well as in emission. The very fact that the system has been observed in absorption shows that the lower state of the system is, most probably, the ground state of the BiCl molecule dissociating into $Bi(^4S_{3/2})$ + $Cl(^2P_{3/2})$ atoms which are the ground states of bismuth and chlorine atoms respectively. The dissociation energies of the upper and the lower states of the system can not be determined accurately as the convergence limit of the system is not known. However the linear extrapolation gives a value of $D_o = 24614\ cm^{-1}$ for the lower state of the system which, as mentioned above, is probably also the ground state of the molecule. The present analysis of the band system gives a cubic term for the upper state which involves observed levels upto about v' = 20. The extrapolation involving the cubic term leads to a dissociation energy of $D_o' = 3750\ cm^{-1}$ for the upper state which will then dissociate at $25507 cm^{-1}$. One can not attach much accuracy to these dissociation limits of the upper and lower states as these were obtained

after fairly large extrapolations. However, it is to be noted that the difference between the two extrapolated dissociation limits 25507 cm^{-1} and 24614 cm^{-1} comes out to be 893 cm^{-1} which is quite close to the normal doublet separation of 881 cm^{-1} for the chlorine atom. Therefore, it appears quite likely that the dissociation limit of the upper state is not the same as that of the ground state but probably the next higher one with $Bi(^4S_{3/2}) + Cl(^2P_{1/2})$ as the dissociation products. The next higher dissociation limit corresponding to $Bi(^2D_{3/2}) + Cl(^2P_{3/2})$ is expected to be at about 35910 cm^{-1} which is much too high for the present upper state to dissociate into. The reasons for taking $Bi(^4S_{3/2}) + Cl(^2P_{1/2})$ as the dissociation products for the upper state are the following:

The present analysis shows the position of the level with V'= 18 at 24855 cm^{-1} which has $\Delta G_{(v+\frac{1}{2})} \simeq 104.8 cm^{-1}$ whereas the dissociation limit by linear extrapolation for the lower state is at 24614 cm^{-1}. This value probably represents the maximum limit for Do" as the linear extrapolation for a non-ionic state is supposed to give a D_o value higher than the actual one. If, however, the upper state is to dissociate at 24614 cm^{-1}, a cubic term with a coefficient of about 0.07 has to be introduced whereas the analysis does not warrant such a high coefficient. Further it will be difficult to explain the observed isotopic shifts if another alternative analysis is chosen such that the upper state dissociates at 24614 cm^{-1}.

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CHAPTER IV.

Emission spectrum of Bismuth Monochloride.

Part II.

The rotational structure and the involved electronic Transition of the band system 6170-4220A.

The Emission Spectrum of BiCl.

Part II: The Rotational Structure and the Involved electronic transition of the Band System 6170 - 4220A.

Abstract.

The rotational structure of the BiCl bands has been obtained for the first time and the rotational lines of four bands (0,2), (0,3), (0,4) and (1,2) have been analysed. The molecular constants obtained are:

$B_0' = 0.0718_0\ cm^{-1}$ $B_1' = 0.0702_{\ } cm^{-1}$

$B_2'' = 0.0838_5\ cm^{-1}$ $B_3'' = 0.0830_{\ } cm^{-1}$ $B_4'' = 0.0827_{\ } cm^{-1}$

$B_0' = 0.0726_{\ } cm^{-1}$ $B_0'' = 0.0850_{\ } cm^{-1}$ $\alpha_e' = (0.0016)$

$\alpha_0'' = (0.0005)$

$r_0' = 2.78_4 \times 10^{-8} cms$ $r_e'' = 2.57_{\ } \times 10^{-8} cms$ $I_0' = 385.4 \times 10^{-40}\ gms\ cm^2$

$I_0'' = 327.3 \times 10^{-40}\ gms\ cm^2$

A detailed consideration of the electronic configuration and the probable low-lying electronic states is given. This along with the experimental observation that only P and R branches occur in the rotational structure, shows that the coupling in the molecule is probably of the Hund's case (c) type and that the electronic transition involved in the emission of the system is probably

$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)^3\Sigma^-(0^+) \longleftarrow (z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^3(v\pi)(u\sigma)^1$

Introduction.

The vibrational analysis of the system 6170-4220A of BiCl obtained by exciting $BiCl_3$ with an uncondensed transformer discharge has been discussed in the previous chapter. It was found that practically all the absorption bands obtained by Morgan are identical with a corresponding number of those in emission in the same region obtained in the present experiments. This made it clear that the band system obtained in the present experiments in emission is very probably the same as the one obtained by Morgan in absorption. Morgan photographed the absorption bands in the first and second orders of a 21-ft grating spectrograph having a grating with 30,000 lines/inch----------

FIGURE I.

The enlargement of bands in the region 4600-4850A bands of BiCl taken on the first order of a 21-ft grating spectrograph.

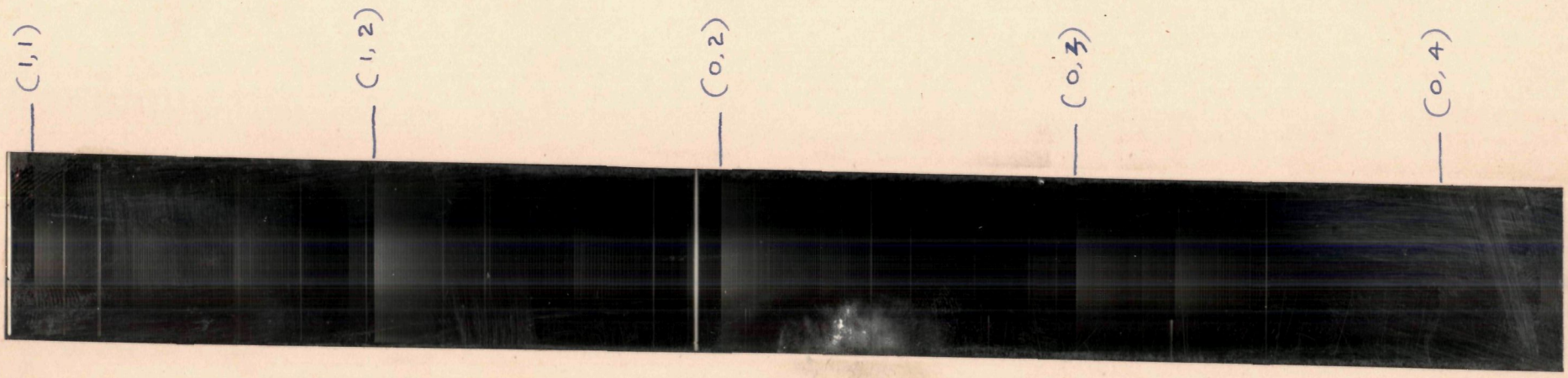


FIGURE 2(a).

The enlargement of the (0,2) band of the 6170-4220A system of BiCl.

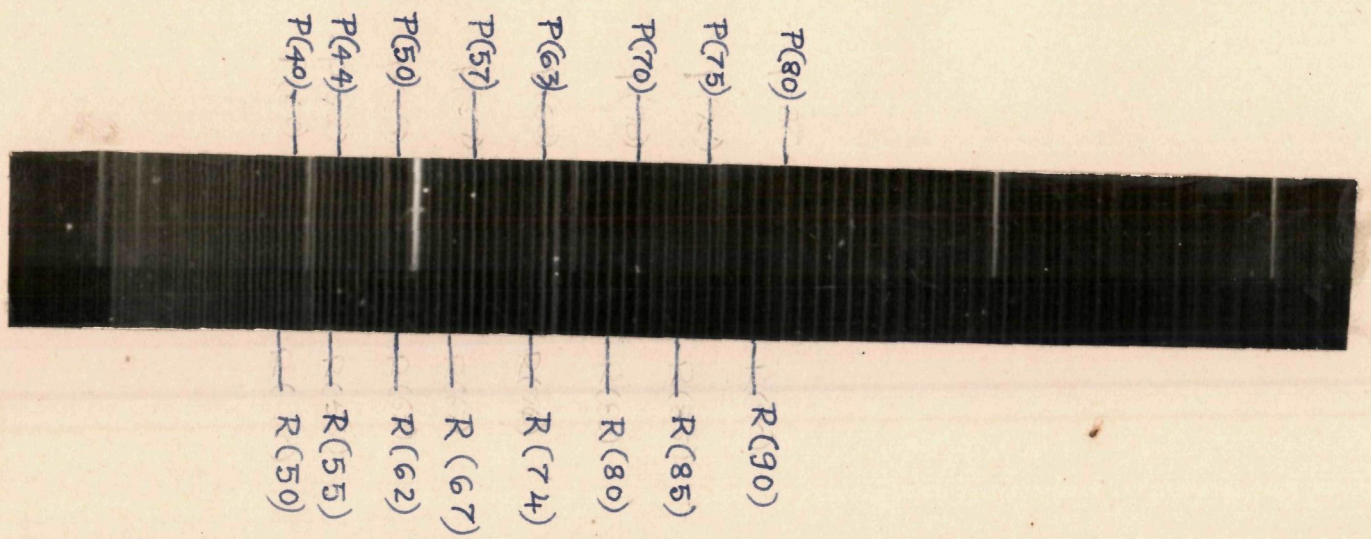


FIGURE 2(b).

The enlargement of the (0,3) band of the 6170-4220A system of BiCl.

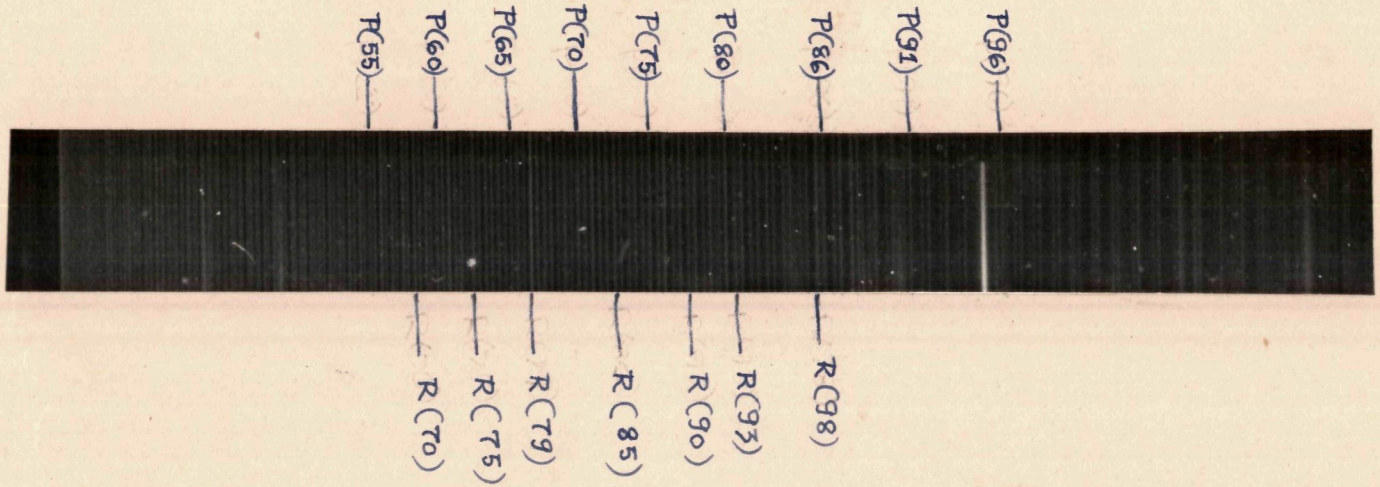


FIGURE 2(c).

The enlargement of the (0,4) band of the 6170-4220A system of BiCl.

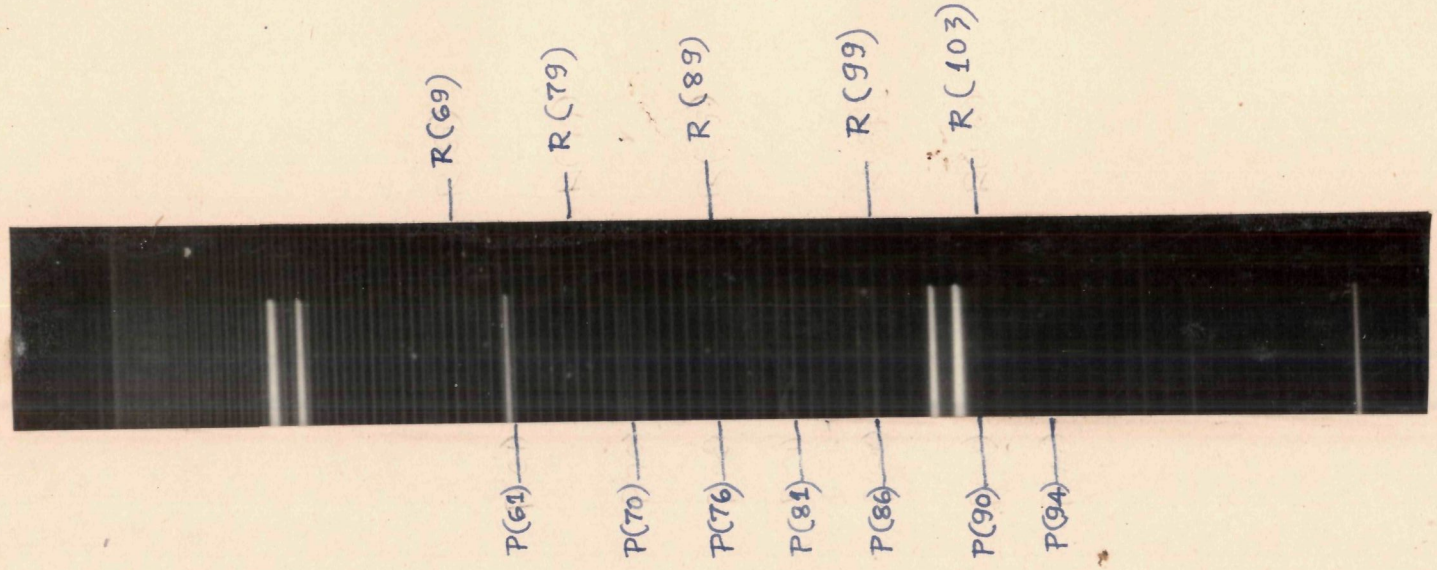
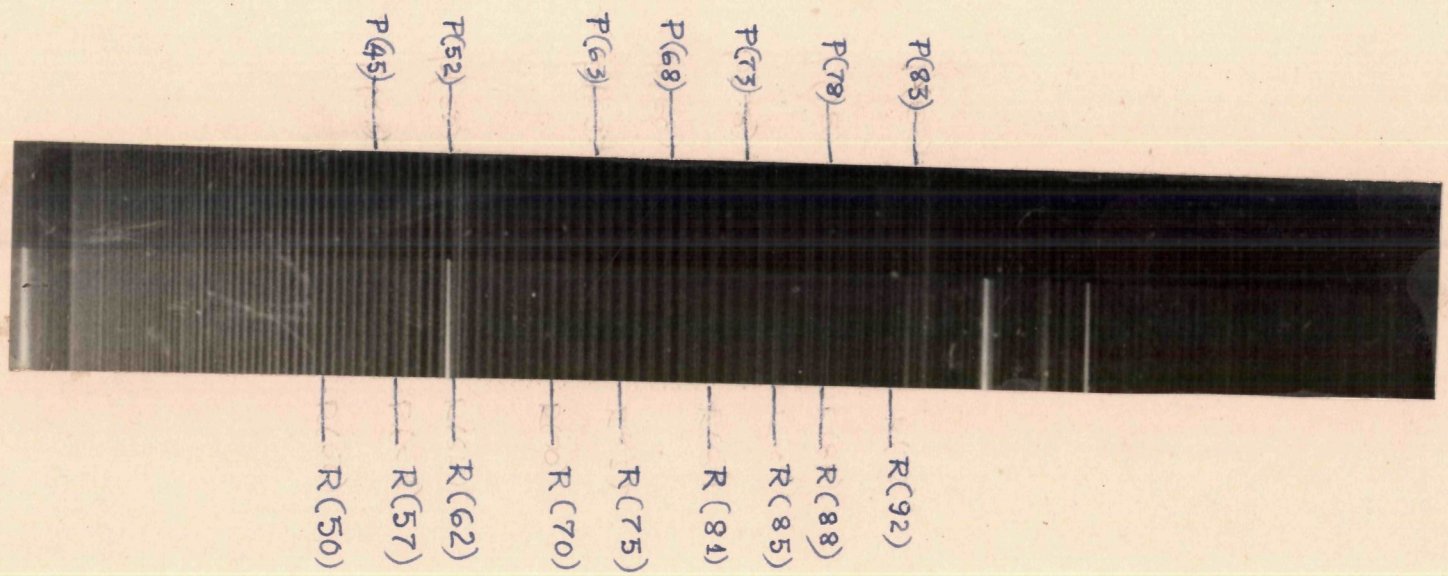


Figure 2(d).

The enlargement of the (1,2) band of the 6170-4220A system of BiCl.



and reported that no rotational structure was revealed. But in the present experiments, where the emission bands are photographed with a 21-ft grating spectrograph having only 15,000 lines/inch, the first order plates show the rotational structure partially resolved while the second order plates show the rotational structure completely well resolved for high J values for some of the bands which are free from overlapping. The dispersion in the second order of the present spectrograph is 1.25A/m.m while that in the case of the spectrograph used by Morgan is 0.8A/m.m. The reason why the rotational structure was not revealed in Morgan's experiments is probably the broadening of the spectral lines caused by the effect due to the high temperatures used in the range 700° K-1400° K and also due to the absorption tube being kept open to the atmosphere which thereby causes the collision with foreign gas molecules at atmospheric pressure.

The rotational analysis of ~~five~~ four bands (0, 2), (0, 3), (0, 4), ~~(1, 1)~~ and (1, 2) are given in this chapter along with the corresponding discussion. The electronic transitions involved in the system ~~is~~ is also discussed.

Experimental Data and Rotational Analysis.

The enlargements of the spectra photographed in the first and second orders of the 21-ft grating spectrograph are shown respectively in figures 1 and 2. The wavenumbers of the rotational lines in the P and R branches of

the bands (0, 2), (0, 3), (0, 4) and (1, 2) are given in tables I to 4 . The bands are well resolved only for high values of J. Herzberg[2] has discussed well the procedure for the determination of the numbering of the rotational lines in the branches of the incompletely resolved bands. If the rotational structure of two different bands which are known to have the same upper ~~rotational~~ vibrational state are studied, then for the correct relative numbering of the rotational lines of the bands considered, the combination differences $R(J) - P(J) = \Delta_2 F'(J)$ must agree exactly for each J value in both the bands. This is a sensitive criterion of whether or not the correct relative numbering has been found. If the bands have the same lower state, the combination differences, $R(J - 1) - P(J + 1) = \Delta_2 F''(J)$ must agree exactly for each J value in both bands. Following the regular procedure involving a number of trials the correct relative numbering of the rotational lines of all the four bands in the present experiments has been fixed. This is clear from table V where the combination differences $\Delta_2 F'$ are shown to agree for each J value in the three bands (0, 2), (0, 3) and (0, 4). The combination differences $\Delta_2 F''$ can also be see to agree for each J value in the bands (0, 2) and (1, 2).

Neglecting in the first instance the centrifugal stretching constant D_v, it can be seen that[2]

TABLE I ROTATIONAL ANALYSIS OF THE (0, 2) BAND:

	a	b	c	d	e	f	g	h	i	j	k	l
J	R(J)	P(J)	$\Delta_2 F'(J)$	$\Delta_2 F''(J)$	$\frac{\Delta_2 F'(J)}{J+\frac{1}{2}}$	$\frac{\Delta_2 F''(J)}{J+\frac{1}{2}}$	$8 D'_{2x}(J+\frac{1}{2})^3$	$\Delta_2 F'(J) + 8 D'_{2x}(J+\frac{1}{2})^3$	$\frac{\Delta_2 F'(J) + 8 D'_{2x}(J+\frac{1}{2})^3}{J+\frac{1}{2}}$	$8 D''_{2x}(J+\frac{1}{2})^3$	$\Delta_2 F''(J) + 8 D''_{2x}(J+\frac{1}{2})^3$	$\frac{\Delta_2 F''(J) + 8 D''_{2x}(J+\frac{1}{2})^3}{J+\frac{1}{2}}$
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
40	21131.65	21120.13	11.41	13.32	.28247	.33029	.0161	11.4561	.28287	.0131	13.3331	.33062
41	30.81	18.04	11.37	13.75	.28843	.33135	.0173	11.3873	.28885	.0141	13.7641	.33186
42	29.94	17.38	12.00	14.15	.28376	.33316	.0186	12.0786	.28420	.0151	14.1751	.33353
43	29.07	16.63	12.42	14.40	.28552	.33103	.0199	12.4399	.28597	.0138	14.4102	.33141
44	28.22	15.51	12.88	14.70	.28494	.33034	.0208	12.7008	.28540	.0165	14.7165	.33071
45	27.13	14.37	12.81	15.22	.28154	.33450	.0229	12.8328	.28204	.0135	15.2335	.33491
46	26.24	13.00	13.24	15.11	.28173	.33130	.0243	13.2643	.28326	.0136	15.1298	.33182
47	25.35	11.77	13.58	15.75	.28539	.33158	.0260	13.6058	.28644	.0211	15.7711	.33202
48	24.31	10.43	13.92	16.12	.28435	.33237	.0276	13.9476	.28552	.0224	16.1424	.33263
49	23.40	09.23	14.17	16.47	.28326	.33273	.0293	14.1988	.28455	.0239	16.4938	.33321
50	22.22	07.84	14.33	16.89	.28476	.33445	.0311	14.4111	.28587	.0253	16.9153	.33496
51	21.24	06.51	14.73	17.19	.28602	.33304	.0330	14.7630	.28666	.0218	17.1268	.33253
52	20.17	05.12	15.06	17.60	.28666	.33524	.0350	15.0850	.28733	.0285	17.6285	.33578
53	18.91	03.84	15.30	17.96	.28411	.33551	.0370	15.2370	.28480	.0301	17.9301	.33603
54	17.88	02.32	15.56	18.05	.28734	.33119	.0391	15.5991	.28806	.0318	18.0318	.33178
55	16.65	00.79	15.76	18.51	.28396	.33351	.0413	15.8013	.28471	.0336	18.5436	.33412
56	15.51	21099.37	16.17	19.03	.28619	.33581	.0436	16.2136	.28697	.0355	19.0655	.33744
57	14.37	97.93	16.73	19.29	.29130	.33543	.0460	16.7359	.29210	.0374	19.3274	.33613

Table:I Continued:-

J	a	b	c	d	e	f	g	h	i	j	k	l
58	21113.30	21099.35	19.73	19.59	.28632	.33407	.0484	18.7804	.28715	.0394	19.3294	.33554
59	11.77	94.78	18.89	19.55	.28555	.33331	.0509	17.0109	.28640	.0414	19.8814	.33431
60	10.40	93.16	17.34	20.20	.28661	.33368	.0535	17.3335	.28719	.0435	20.2435	.33439
61	09.23	91.87	17.88	20.61	.28715	.33512	.0562	17.7162	.28807	.0457	20.6557	.33596
62	07.84	89.68	17.96	20.87	.28736	.33382	.0590	18.0190	.28839	.0480	20.9180	.33469
63	06.51	86.36	18.15	21.36	.28583	.33490	.0619	18.2119	.28690	.0503	21.3103	.33559
64	05.12	85.59	18.51	21.60	.28744	.33485	.0648	18.6018	.28844	.0527	21.6527	.33570
65	03.64	84.91	18.73	21.89	.28595	.33419	.0679	18.7979	.28699	.0552	21.9452	.33504
66	02.22	83.23	18.99	22.23	.28586	.33428	.0711	19.0611	.28663	.0578	22.2878	.33515
67	00.79	81.41	19.33	22.58	.28711	.33452	.0743	19.4543	.28821	.0605	22.6405	.33541
68	21099.37	79.64	19.73	22.93	.28803	.33471	.0777	19.8077	.28919	.0632	22.9932	.33567
69	97.82	77.92	19.79	23.33	.28472	.33568	.0811	19.8411	.28545	.0660	23.3960	.33663
70	96.26	76.04	20.21	23.42	.28666	.33319	.0847	20.2947	.28787	.0689	23.4389	.33317
71	94.73	74.20	20.59	23.88	.28783	.33398	.0883	20.6653	.28907	.0719	23.8519	.33439
72	93.15	72.37	20.79	24.35	.28662	.33586	.0921	20.8721	.28789	.0749	24.4249	.33689
73	91.57	70.13	21.14	24.61	.28762	.33483	.0959	21.2359	.28892	.0781	24.8381	.33589
74	89.98	68.54	21.31	24.97	.28644	.33517	.0999	21.4399	.28773	.0813	25.2513	.33626
75	88.36	66.60	21.76	25.22	.28821	.33404	.1040	21.9610	.28950	.0846	25.5046	.33516
76	86.53	64.86	21.93	25.76	.28654	.33673	.1082	22.0832	.28785	.0880	25.9480	.33788
77	84.91	62.80	22.31	26.00	.28787	.33549	.1125	22.4225	.28932	.0915	26.0915	.33669

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Table I Continued:-

J	a	b	c	d	e	f	g	h	i	j	k	l
78	21083.23	21060.58	22.65	26.37	.28853	.33592	.1169	22.7669	.29002	.0951	26.4651	.33713
79	81.41	58.54	22.87	26.72	.28767	.33610	.1214	22.3914	.28920	.0985	26.8188	.33734
80	79.34	56.51	23.13	27.00	.28733	.33540	.1260	23.2560	.28889	.1026	27.1026	.33663
81	77.86	54.41	23.45	27.39	.28773	.33607	.1309	23.5808	.28933	.1064	27.4964	.33738
82	76.04	52.25	23.79	27.78	.28836	.33673	.1357	23.9257	.28901	.1104	27.8904	.33806
83	74.20	50.08	24.12	28.11	.28886	.33664	.1407	24.2607	.29055	.1145	28.2245	.33802
84	72.37	47.93	24.44	28.44	.28923	.33657	.1459	24.5958	.29096	.1190	28.5586	.33797
85	70.48	45.76	24.87	28.80	.28854	.33684	.1510	24.8210	.29030	.1229	28.9229	.33826
Average					.28678	.33476			.28742			.33516

TABLE: II ROTATIONAL ANALYSIS OF THE (0, 3) BAND

	a	b	c	d	e	f	g	h	i	j	k	l
J	R(J)	P(J)	$\Delta_2F'(J)$	$\Delta_2F''(J)$	$\frac{\Delta_2F'(J)}{J+\frac{1}{2}}$	$\frac{\Delta_2F''(J)}{J+\frac{1}{2}}$	$8D'_u(J+\frac{1}{2})^3$	$\Delta_2F'(J)+8D'_u(J+\frac{1}{2})^3$	$\frac{\Delta_2F'(J)+8D'_u(J+\frac{1}{2})^3}{J+\frac{1}{2}}$	$8D''_u(J+\frac{1}{2})^3$	$\Delta_2F''(J)+8D''_u(J+\frac{1}{2})^3$	$\frac{\Delta_2F''(J)+8D''_u(J+\frac{1}{2})^3}{J+\frac{1}{2}}$
	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}	in cm^{-1}
57	20814.25	20797.88	16.37	18.96	.28469	.32974	.0459	16.4159	.28549	.0368	18.9968	.33038
58	13.07	96.36	16.69	19.33	.28530	.33043	.0484	16.7384	.28613	.0388	19.3688	.33109
59	11.90	94.92	16.98	19.65	.28538	.32857	.0509	17.0309	.28623	.0408	19.5908	.32926
60	10.67	93.52	17.15	20.01	.28347	.33074	.0535	17.2035	.28435	.0429	20.0529	.33145
61	09.42	91.89	17.53	20.23	.28504	.32894	.0562	17.5862	.28595	.0451	20.2751	.32967
62	08.17	90.44	17.73	20.55	.28368	.32880	.0590	17.7890	.28462	.0473	20.5973	.32956
63	06.80	88.87	17.99	20.97	.28331	.33024	.0619	18.0519	.28428	.0496	21.0196	.33102
64	05.57	87.20	18.37	21.34	.28481	.33085	.0648	18.4348	.28581	.0520	21.3920	.33166
65	04.27	85.52	18.75	21.64	.28626	.33038	.0679	18.8179	.28729	.0544	21.6944	.33121
66	02.94	83.93	19.01	21.98	.28586	.33053	.0711	19.0811	.28693	.0570	22.0370	.33138
67	01.48	82.29	19.19	22.37	.28430	.33141	.0743	19.2843	.28539	.0596	22.4296	.33229
68	00.14	80.57	19.57	22.61	.28569	.33007	.0777	19.6477	.28683	.0623	22.6723	.33098
69	20796.71	78.87	19.84	23.08	.28587	.33180	.0811	19.9211	.28663	.0650	23.1250	.33273
70	97.19	77.08	20.11	23.36	.28525	.33135	.0847	20.1947	.28645	.0679	23.4279	.33231
71	95.76	75.35	20.41	23.81	.28545	.33007	.0883	20.4983	.28669	.0709	23.8309	.33120
72	94.28	73.58	20.68	23.97	.28524	.33062	.0921	20.7721	.28651	.0739	24.0439	.33164
73	92.81	71.70	21.02	24.28	.28599	.33034	.0958	21.1159	.28729	.0769	24.3569	.33138
74	91.18	69.98	21.20	24.71	.28456	.33168	.0999	21.2999	.28590	.0801	24.7901	.33275
75	89.15	68.10	21.05	25.02	.27881	.33139	.1040	21.1540	.28018	.0834	25.1034	.33249
76	88.09	66.16	21.93	24.85	.28666	.32484	.1082	22.0382	.28803	.0867	24.9367	.32597

Table: I Continued:-

J	a	b	c	d	e	f	g	h	i	j	k	l
77	20786.35	20764.30	22.05	25.75	.28452	.33226	.1126	22.1625	.28587	.0902	25.6402	.33342
78	84.83	62.34	22.49	25.93	.28649	.33032	.1103	22.6069	.28790	.0937	26.0237	.33151
79	83.14	60.42	22.72	26.43	.28579	.33245	.1214	22.8414	.28731	.0974	26.5274	.33368
80	81.42	58.40	23.02	26.79	.28596	.33160	.1200	23.1460	.28753	.1011	26.8011	.33293
81	79.75	56.44	23.32	27.01	.28618	.33141	.1306	23.1503	.28774	.1049	27.1149	.33270
82	77.93	54.41	23.52	27.43	.28509	.33248	.1357	23.3557	.28674	.1098	27.5386	.33380
83	76.25	52.33	23.92	27.83	.28647	.33059	.1407	23.8607	.28815	.1128	27.7423	.33225
84	74.49	50.30	24.19	28.08	.28697	.33231	.1456	24.3358	.28800	.1169	28.1369	.33369
85	72.89	48.47	24.42	28.41	.28691	.33229	.1513	24.5716	.28798	.1211	28.5311	.33370
86	70.87	46.08	24.79	28.87	.28653	.33144	.1564	24.9464	.28840	.1254	28.7854	.33283
87	69.03	43.92	25.11	29.13	.28697	.33291	.1613	25.2719	.28838	.1298	29.2599	.33440
88	67.06	41.74	25.32	29.55	.28610	.33267	.1675	25.4975	.28799	.1343	29.6245	.33519
89	65.21	39.59	25.71	29.79	.28722	.33184	.1732	25.8832	.28830	.1388	29.8388	.33339
90	63.26	37.36	25.89	30.11	.28697	.33271	.1791	26.0891	.28808	.1436	30.2536	.33429
91	61.28	35.19	26.18	30.34	.28712	.33158	.1851	26.3851	.28811	.1484	30.4884	.33321
92	59.39	32.91	26.39	30.73	.28630	.33222	.1912	26.6812	.28730	.1534	30.8834	.33387
93	57.31	30.85	26.76	31.05	.28620	.33208	.1975	26.9575	.28831	.1581	31.2081	.33373
94	55.27	28.25	27.02	31.33	.28693	.33153	.2038	27.2239	.28809	.1635	31.4935	.33326
Average					.28549	.33062			.28689			.33234

TABLE: III ROTATIONAL ANALYSIS OF THE (0, 1) BAND

	a	b	c	d	e	f	g	h	i	j	K	l
J	R(J) in cm^{-1}	P(J) in cm^{-1}	$\Delta_2F'(J)$ in cm^{-1}	$\Delta_2F''(J)$ in cm^{-1}	$\frac{\Delta_2F'(J)}{J+\frac{1}{2}}$ in cm^{-1}	$\frac{\Delta_2F''(J)}{J+\frac{1}{2}}$ in cm^{-1}	$\delta D_u' \times (J+\frac{1}{2})^3$ in cm^{-1}	$\Delta_2F'(J) + \delta D_u'(J+\frac{1}{2})^3$ in cm^{-1}	$\frac{\Delta_2F'(J)+\delta D_u'(J+\frac{1}{2})^3}{J+\frac{1}{2}}$ in cm^{-1}	$\delta D_u''(J+\frac{1}{2})^3$ in cm^{-1}	$\Delta_2F''(J)+\delta D_u''(J+\frac{1}{2})^3$ in cm^{-1}	$\frac{\Delta_2F''(J)+\delta D_u''(J+\frac{1}{2})^3}{J+\frac{1}{2}}$ in cm^{-1}
50	20522.14	20507.74	14.40	16.46	.28515	.32594	.0311	14.4345	.28583	.0245	16.4345	.32642
51	21.04	06.56	14.48	16.93	.28116	.32873	.0330	14.5130	.28180	.0259	16.9550	.32934
52	20.57	06.21	14.86	17.13	.28305	.32629	.0350	14.8950	.28371	.0275	17.1575	.32681
53	19.14	05.31	15.19	17.51	.28393	.32723	.0370	15.2270	.28463	.0291	17.5391	.32783
54	18.01	02.50	15.45	17.88	.28349	.32807	.0391	15.4891	.28420	.0307	17.9107	.32864
55	17.09	01.22	15.78	18.13	.28472	.32667	.0413	15.8213	.28507	.0323	18.1623	.32725
56	16.90	20499.85	16.02	18.50	.28353	.32743	.0436	16.0836	.28431	.0343	18.5243	.32804
57	14.86	98.50	16.35	18.84	.28435	.32765	.0459	16.3959	.28515	.0361	18.8761	.32826
58	13.71	97.06	16.65	19.18	.28462	.32756	.0484	16.6984	.28541	.0380	19.2180	.32851
59	12.59	95.87	16.93	19.51	.28396	.32768	.0509	16.9309	.28471	.0400	19.5500	.32857
60	11.10	94.20	17.20	19.77	.28429	.32677	.0535	17.2535	.28518	.0421	19.8121	.32747
61	10.13	92.73	17.49	20.26	.28298	.32943	.0562	17.4562	.28391	.0442	20.3042	.33015
62	08.98	91.14	17.81	20.47	.28496	.32752	.0590	17.8690	.28590	.0464	20.5164	.32826
63	07.74	89.68	18.08	20.84	.28472	.32831	.0619	18.1419	.28579	.0488	20.8936	.32108
64	06.56	88.61	17.95	21.22	.27629	.32899	.0648	18.0148	.27930	.0510	21.2710	.32978
65	05.21	86.52	18.69	21.64	.28534	.33038	.0678	18.7578	.28658	.0534	21.6934	.33120
66	03.91	84.92	18.99	21.88	.28556	.32902	.0711	19.0611	.28663	.0558	21.9358	.32986
67	02.56	83.33	19.23	22.21	.28489	.32904	.0743	19.3043	.28589	.0584	22.2684	.32990
68	01.22	81.70	19.52	22.56	.28496	.32919	.0777	19.5977	.28610	.0610	22.6110	.33008
69	20499.88	80.01	19.87	22.92	.28589	.33078	.0811	19.9511	.28707	.0638	22.9838	.33070
70	98.60	78.30	20.20	23.27	.28652	.33007	.0847	20.2847	.28773	.0665	23.3365	.33101
71	97.03	76.61	20.45	23.65	.28601	.33077	.0883	20.5383	.28725	.0694	23.7194	.33174
72	95.37	74.85	20.62	23.97	.28717	.33062	.0921	20.9121	.28841	.0724	24.0424	.33162

Table: III Continued:-

J	a	b	c	d	e	f	g	h	i	j	k	l
73	20494.20	20473.09	21.11	24.34	.28721	.33116	.0959	21.2059	.28851	.0754	24.4154	.33218
74	92.73	71.33	21.40	24.76	.28725	.33235	.0999	21.4999	.28859	.0785	24.8385	.33340
75	91.14	69.44	21.70	25.09	.28742	.33232	.1040	21.8040	.28879	.0817	25.1717	.33340
76	89.66	67.64	22.02	25.43	.28784	.33242	.1082	22.1282	.28926	.0850	25.5150	.33353
77	88.61	65.71	22.90	25.75	.29548	.33226	.1125	23.0125	.29693	.0884	25.8384	.33340
78	86.52	63.91	22.61	26.63	.28803	.33924	.1169	22.7269	.28951	.0919	26.7219	.34040
79	84.92	61.98	22.94	26.46	.28855	.33283	.1214	23.0614	.29008	.0954	26.5554	.33403
80	83.33	60.06	23.27	26.79	.28907	.33279	.1260	23.3960	.29063	.0991	26.8891	.33404
81	81.70	58.13	23.57	27.21	.28920	.33387	.1308	23.7008	.29081	.1028	27.3128	.33525
82	80.01	56.12	23.89	27.54	.28957	.33382	.1357	24.0257	.29122	.1066	27.6466	.33511
83	78.30	54.16	24.14	27.86	.28910	.33365	.1407	24.2607	.29079	.1106	27.9706	.33498
84	76.61	52.15	24.46	28.20	.28947	.33373	.1458	24.6058	.29119	.1146	28.3146	.33508
85	74.85	50.10	24.75	28.53	.28947	.33368	.1510	24.9010	.29124	.1187	28.6487	.33507
86	73.09	48.08	25.01	28.82	.28913	.33318	.1564	25.1664	.29094	.1229	28.9429	.33460
87	71.33	46.03	25.30	29.27	.28914	.33451	.1619	25.4619	.29099	.1272	29.3972	.33597
88	69.44	43.82	25.62	29.52	.28949	.33356	.1675	25.7875	.29138	.1316	29.6516	.33505
89	67.64	41.81	25.83	29.76	.28860	.33251	.1732	26.0032	.29054	.1362	29.8962	.33404
90	65.71	39.68	26.03	30.12	.28762	.33282	.1791	26.2091	.28960	.1408	30.2608	.33437
Average					.28647	.33058			.28752			.33115

TABLE IV ROTATIONAL ANALYSIS OF THE (1, 2) BAND.

	a	b	c	d	e	f	g	h	i	j	k	l
J	R(J)	P(J)	$\Delta_2 F'(J)$	$\Delta_2 F''(J)$	$\frac{\Delta_2 F'(J)}{J+\frac{1}{2}}$	$\frac{\Delta_2 F''(J)}{J+\frac{1}{2}}$	$BD'_u(J+\frac{1}{2})^3$	$\Delta_2 F'(J) + BD'_u(J+\frac{1}{2})^3$	$\frac{\Delta_2 F'(J) + BD'_u(J+\frac{1}{2})^3}{J+\frac{1}{2}}$	$BD''_u(J+\frac{1}{2})^3$	$\Delta_2 F''(J) + BD''_u(J+\frac{1}{2})^3$	$\frac{\Delta_2 F''(J) + BD''_u(J+\frac{1}{2})^3}{J+\frac{1}{2}}$
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
40	21387.86	21326.14	11.72	14.00	.28976	.34636	.0151	11.7351	.28975	.0131	14.0131	.34600
41	36.76	24.01	11.95	14.38	.28736	.34008	.0162	11.9562	.28634	.0141	14.3741	.34635
42	35.70	23.50	12.20	14.66	.28703	.34404	.0175	12.2175	.28747	.0151	14.6751	.34530
43	34.63	22.10	12.52	14.97	.28805	.34372	.0188	12.5488	.28648	.0162	14.9462	.34359
44	33.49	20.77	12.86	15.30	.28404	.34369	.0191	12.8801	.28537	.0165	15.3165	.34419
45	32.31	19.53	12.96	15.64	.28527	.34154	.0218	13.0018	.28575	.0196	15.5565	.34194
46	31.05	17.31	13.14	15.77	.28259	.33914	.0228	13.1528	.28307	.0196	15.7595	.33956
47	29.93	16.51	13.39	15.99	.28189	.33643	.0241	13.4146	.28241	.0211	16.0011	.33686
48	28.70	15.07	13.63	16.43	.28103	.33913	.0250	13.6560	.28157	.0224	16.4724	.33964
49	27.41	13.48	13.93	16.74	.28141	.33813	.0276	13.9576	.28197	.0236	16.7636	.33866
50	26.14	11.96	14.13	16.97	.28079	.33604	.0293	14.2093	.28137	.0253	16.9953	.33654
51	24.81	10.44	14.37	17.30	.27905	.33632	.0311	14.4011	.27903	.0266	17.3266	.33644
52	23.50	08.84	14.66	17.63	.27924	.33390	.0330	14.6930	.27957	.0285	17.6585	.33445
53	22.10	07.39	14.93	18.01	.27701	.33664	.0349	14.9549	.27768	.0301	18.0401	.33720
54	20.77	05.49	15.26	18.18	.27836	.33321	.0369	15.3169	.28104	.0318	18.1918	.33379
55	19.33	03.94	15.59	18.54	.27723	.33015	.0389	15.4789	.27800	.0336	18.5736	.33105
56	17.91	02.43	15.48	18.83	.27396	.33327	.0411	15.5211	.27471	.0355	18.8855	.33390
57	16.34	00.50	16.04	19.39	.27896	.33722	.0433	16.0833	.27971	.0374	19.4274	.33735

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Table IV Continued-

J	a	b	c	d	e	f	g	h	i	j	k	l
58	21313.07	21298.52	16.55	19.89	.28291	.33658	.0456	16.5856	.28366	.0394	19.7294	.33725
59	13.40	96.65	16.03	19.87	.27949	.33563	.0460	16.6760	.28030	.0414	20.0114	.33633
60	11.98	95.19	16.30	20.29	.27867	.33537	.0505	16.6105	.27951	.0435	20.3333	.33609
61	10.44	93.19	17.25	20.55	.28049	.33414	.0530	17.3030	.28135	.0457	20.5957	.33490
62	08.31	91.11	17.43	20.91	.27858	.33296	.0566	17.1666	.27977	.0490	20.9590	.33373
63	07.28	89.03	17.05	21.11	.27795	.33244	.0583	17.7035	.27837	.0503	21.1803	.33323
64.	05.49	87.73	17.78	21.52	.27534	.33364	.0611	17.8211	.27829	.0527	21.5727	.33443
65	03.94	85.75	18.10	21.83	.27755	.33099	.0640	18.0440	.27855	.0552	21.8582	.33184
66	02.43	83.81	18.02	22.12	.28000	.33263	.0670	18.6970	.28101	.0573	22.1775	.33350
67	00.50	81.82	18.68	22.59	.27674	.33108	.0701	18.7681	.27778	.0605	22.5535	.33156
68.	21298.93	79.81	19.09	22.96	.27816	.33080	.0732	19.1332	.27975	.0632	22.7232	.33172
69	97.25	77.84	19.41	23.11	.27926	.33252	.0765	19.4005	.28038	.0660	23.1765	.33347
70	95.46	75.85	19.54	23.45	.27858	.33212	.0793	19.7193	.27971	.0690	23.5183	.33360
71	93.72	73.80	19.92	23.87	.27860	.33196	.0853	20.0033	.27977	.0719	23.7410	.33205
72.	91.31	71.79	20.12	24.13	.27752	.33286	.0868	20.2005	.27871	.0749	24.2049	.33386
73	90.08	69.59	20.49	24.19	.27877	.33312	.0905	20.5805	.28001	.0781	24.5981	.33426
74	88.19	67.42	20.83	24.71	.27759	.33188	.0942	20.7742	.27885	.0818	24.7913	.33277
75	86.33	65.37	20.96	25.01	.27762	.33205	.0981	21.0581	.27891	.0846	25.1246	.33277
76	84.35	63.33	21.29	25.45	.27850	.33283	.1020	21.3920	.27983	.0880	25.5380	.33383
77	82.42	60.88	21.65	25.89	.27806	.33148	.1061	21.6581	.27943	.0916	25.7313	.33266

Table: iv Continued:-

J	a	b	c	d	e	f	g	h	i	j	k	l
78	21780.40	21258.66	21.80	26.04	.27777	.3347 2	.1102	21.8102	.27311	.0951	36.1351	.33266
79	73.18	50.79	22.00	26.18	.27748	.33253	.1148	22.1715	.27302	.0988	36.5136	.33257
80	76.36	54.04	22.21	26.72	.27714	.33198	.1139	22.1289	.27362	.1026	36.3826	.33320
81	74.10	52.73	22.37	27.00	.27318	.33185	.1273	22.7333	.27307	.1064	37.1264	.33258
82	72.32	49.35	22.97	27.41	.27812	.33201	.1270	22.0970	.27297	.1104	37.5504	.33304
83	70.95	48.96	23.20	27.71	.27832	.33188	.1326	22.1326	.28051	.1145	37.3246	.33323
84	68.15	44.01	23.52	26.11	.27834	.33202	.1574	23.0574	.27997	.1185	36.3206	.33407
85	66.00	42.14	23.80	26.51	.27906	.33248	.1434	21.0004	.28078	.1220	36.3380	.33489
86	63.62	39.02	24.20	25.35	.27977	.33353	.1173	21.3475	.28147	.1272	36.3772	.33309
87	61.68	37.13	24.51	28.10	.28011	.33357	.1525	21.3733	.28198	.1317	39.2317	.33408
88	59.41	34.72	24.69	29.11	.27898	.33232	.1579	24.8473	.28077	.1363	39.3403	.33386
89	57.19	32.25	24.91	28.69	.27866	.33173	.1633	25.1033	.28048	.1410	39.3510	.33331
90	54.83	29.72	25.17	30.09	.27812	.33238	.1589	25.3389	.27933	.1457	39.2257	.33393
Average					.27979	.33422			.28079			.33368

Table V.

Combination Difference for the different bands studied.

	a (1,2)	b	c (0,2)	d	e (0,3)	f	g (0,4)	h
J	R(J) - P(J)	R(J-1)-P(J+1)	R(J) - P(J)	R(J-1)-P(J+1)	R(J) - P(J)	R(J-1)-P(J+1)	R(J) - P(J)	R(J-1) - P(J+1)
35	10.42	12.63						
36	10.76	12.80						
37	11.00	13.11						
38	11.21	13.52						
39	11.40	13.77						
40	11.72	14.00	11.44	13.62				
41	11.95	14.36	11.97	13.75				
42	12.20	14.66	12.06	14.16				
43	12.53	14.93	12.42	14.40				
44	12.68	15.30	12.68	14.70				
45	12.98	15.54	12.81	15.22				
46	13.14	15.77	13.24	15.41				
47	13.39	15.98	13.58	15.75				
48	13.63	16.45	13.82	16.12				
49	13.93	16.74	14.17	16.47				
50	14.18	16.97	14.38	16.89			14.40	16.46
51	14.37	17.30	14.73	17.10			14.48	16.93
52	14.66	17.53	15.05	17.60			14.86	17.13
53	14.82	18.01	15.20	17.95			15.19	17.51
54	15.28	18.16	15.66	18.05			15.45	17.88
55	15.39	18.34	15.76	18.51			15.78	18.13
56	15.48	18.83	16.17	19.03			16.02	18.50
57	16.04	19.39	16.75	19.29	16.37	18.96	16.35	18.84

Table V* (continued)

J	(1,2) a	b	(0,2) c	d	(0,3) e	f	(0,4) g	h
	m^{-1}	s^{-1}	m^{-1}	s^{-1}	m^{-1}	s^{-1}	m^{-1}	s^{-1}
58	16.55	19.69	16.75	19.59	16.69	19.33	16.65	19.18
59	16.63	19.97	16.99	19.85	16.98	19.55	16.83	19.51
60	16.86	20.29	17.34	20.20	17.15	20.01	17.20	19.77
61	17.25	20.55	17.66	20.61	17.53	20.23	17.40	20.26
62	17.43	20.81	17.96	20.87	17.73	20.55	17.81	20.47
63	17.65	21.11	18.15	21.26	17.99	20.97	18.08	20.34
64	17.76	21.52	18.54	21.60	18.37	21.34	17.95	21.22
65	18.18	21.68	18.73	21.89	18.75	21.64	18.69	21.64
66	18.62	22.12.	18.99	22.23	19.01	21.98	18.99	21.88
67	18.68	22.59	19.38	22.58	19.19	22.37	19.23	22.21
68	10.09	22.66	19.73	22.93	19.57	22.61	19.52	22.55
69	19.41	23.11	19.76	23.33	19.84	23.06	19.87	22.92
70	19.64	23.45	20.21	23.42	20.11	23.36	20.20	23.27
71	19.92	23.67	20.58	23.88	20.41	23.61	20.45	23.65
72	20.12	24.13	20.78	24.35	20.68	23.97	20.82	23.97
73	20.49	24.49	21.14	24.61	21.02	24.28	21.11	24.34
74	20.68	24.71	21.34	24.97	21.20	24.71	21.40	24.76
75	20.96	25.04	21.76	25.22	21.05	25.02	21.70	25.09
76	21.29	25.45	21.92	25.76	21.93	24.85	22.02	25.43
77	21.55	25.69	22.31	26.00	22.05	25.75	22.90	25.75
78	21.80	26.04	22.65	26.37	22.49	25.93	22.61	26.63
79	22.06	26.42	22.87	26.72	22.72	26.43	22.94	26.46
80	22.31	26.72	23.13	27.00	23.02	26.70	23.27	26.79
81	22.67	27.00	23.45	27.39	23.32	27.01	23.57	27.21

Table V (continued)

	(1,2)		(0,2)		(0,3)		(0,4)	
	a	b	c	d	e	f	g	h
82	22.97	27.44	23.79	27.78	23.52	27.43	23.89	27.54
83	23.29	27.71	24.12	28.11	23.92	27.63	24.14	27.86
84	23.52	28.11	24.44	28.44	24.19	28.08	24.46	28.20
85	23.86	28.51	24.67	28.80	24.42	28.41	24.75	28.53
86	24.20	28.85			24.79	28.67	25.01	28.82
87	24.51	29.10			25.11	29.13	25.30	29.27
88	24.69	29.41			25.32	29.53	25.62	29.52
89	24.94	29.69			25.71	29.70	25.83	29.76
90	25.17	30.08			25.89	30.11	26.03	30.12

$$\Delta_2 F(J) = F_v(J+1) - F_v(J-1)$$
$$= B_v(J+1)(J+2) - B_v J(J-1)$$
$$= 4B_v(J+1/2)$$

The combination differences $\Delta_2 F(J)$ form to a first good approximation a linear function of the rotational quantum number J going through zero for $J=-1/2$. This fact had been made use of in the determination of the correct absolute numbering of the rotational lines. If the combination differences are plotted against a preliminary correct relative numbering, the correct absolute numbering is obtained by shifting the abscissa scale, until the straight line form-ed by the $\Delta_2 F$ values goes through the point $J=-\frac{1}{2}$. Such graphs representing the $\Delta_2 F'(J)$ and $\Delta_2 F''(J)$ are shown in Fig. 3 to 6 for the four different bands studied. The numbering given for the rotational lines in tables I to V is the absolute numbering determined from these graphs. The slopes of these curves give to a good approximation the values of $4B''_v$ and $4B'_v$ respectively.

The $4B''_v$ and $4B'_v$ are obtained also by taking the respective mean values of $\frac{\Delta_2 F''(J)}{J+1/2}$ and $\frac{\Delta_2 F'(J)}{J+1/2}$ given in tables I to IV. The values of B''_v and B'_v so calculated are given in table VI.

An attempt has then been made to improve the accuracy in the determination of the values of B_v by taking centrifugal stretching constant into consideration. If

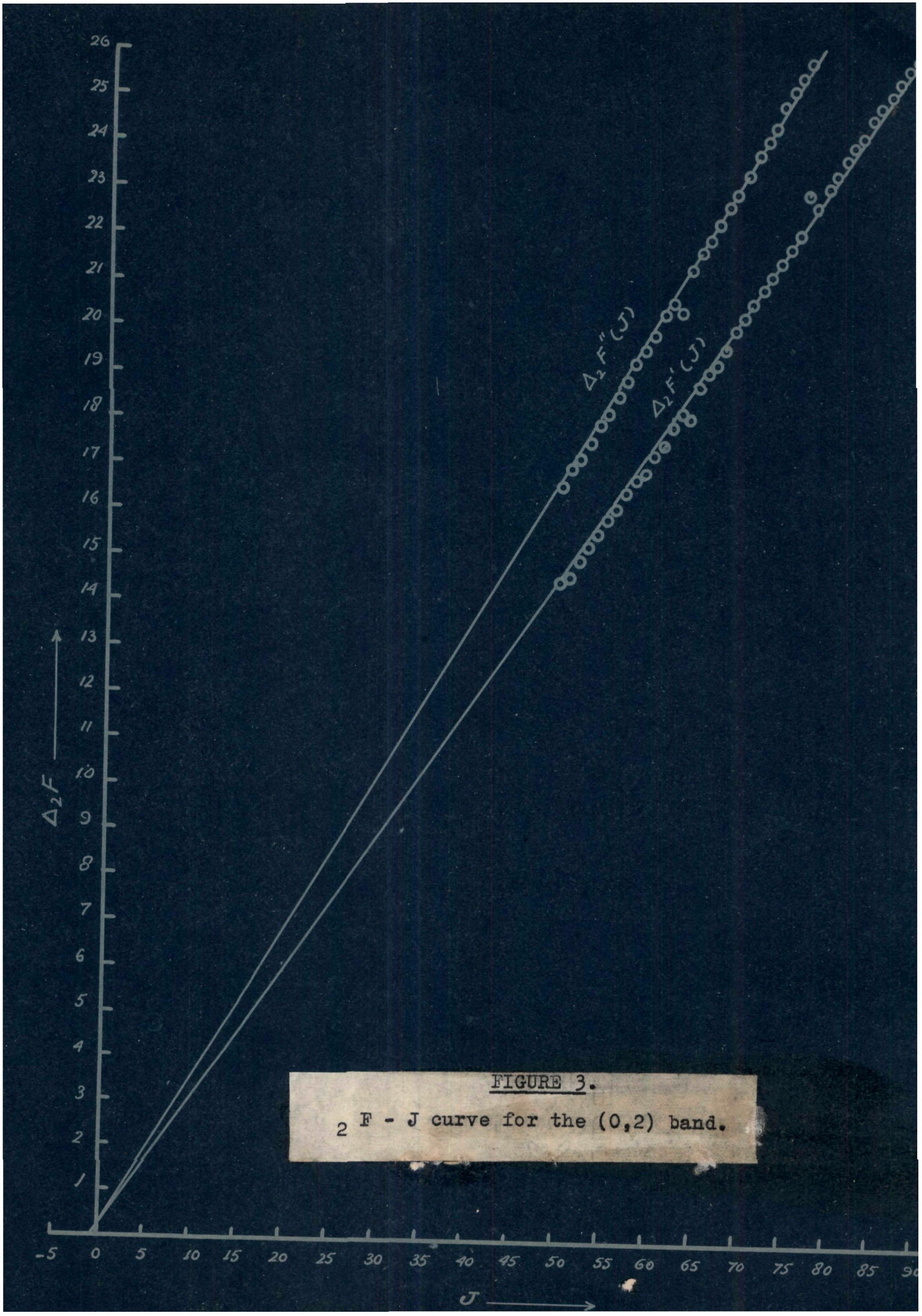

FIGURE 3.

^{2}F - J curve for the (0,2) band.

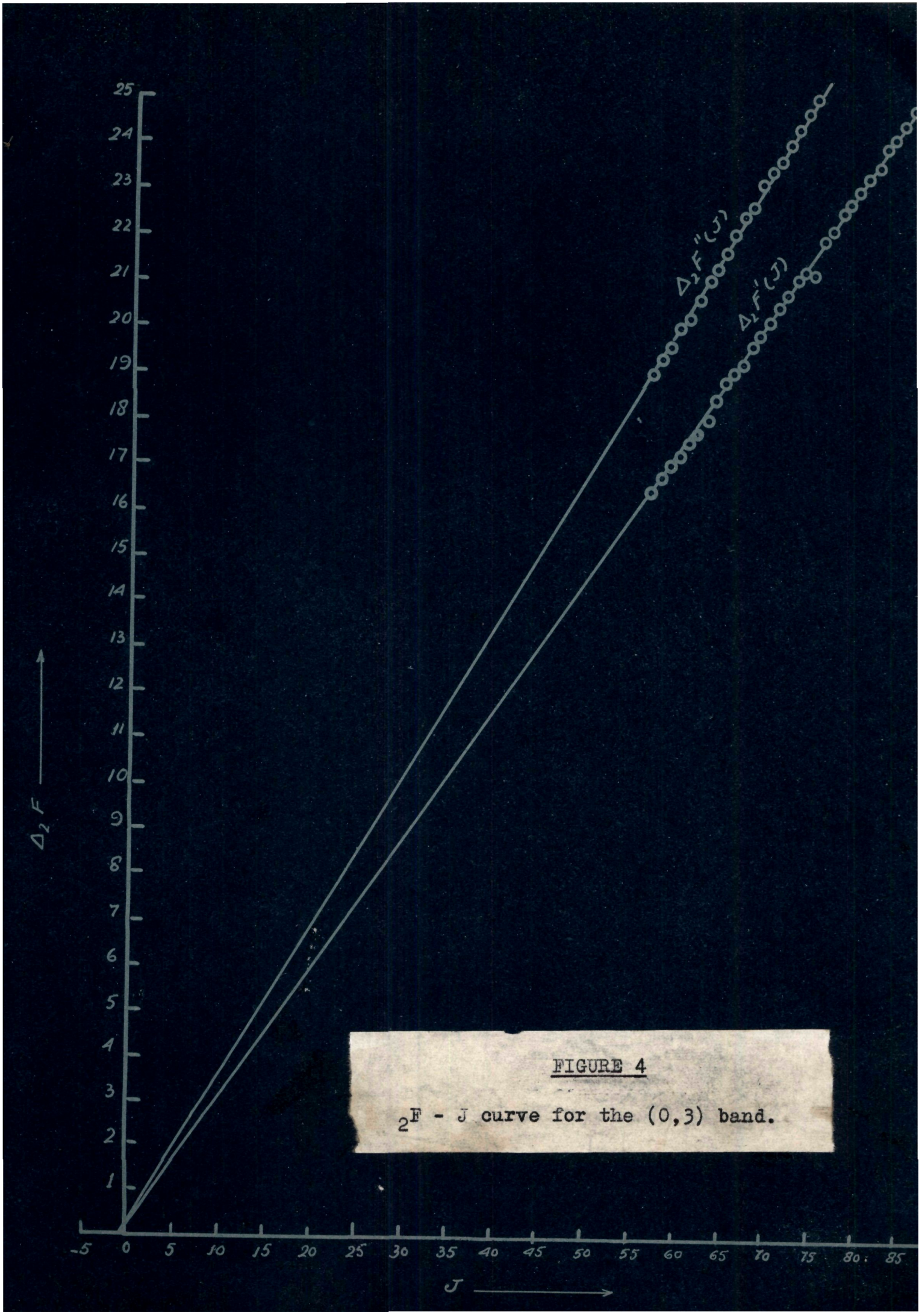

FIGURE 4

^2F - J curve for the (0,3) band.

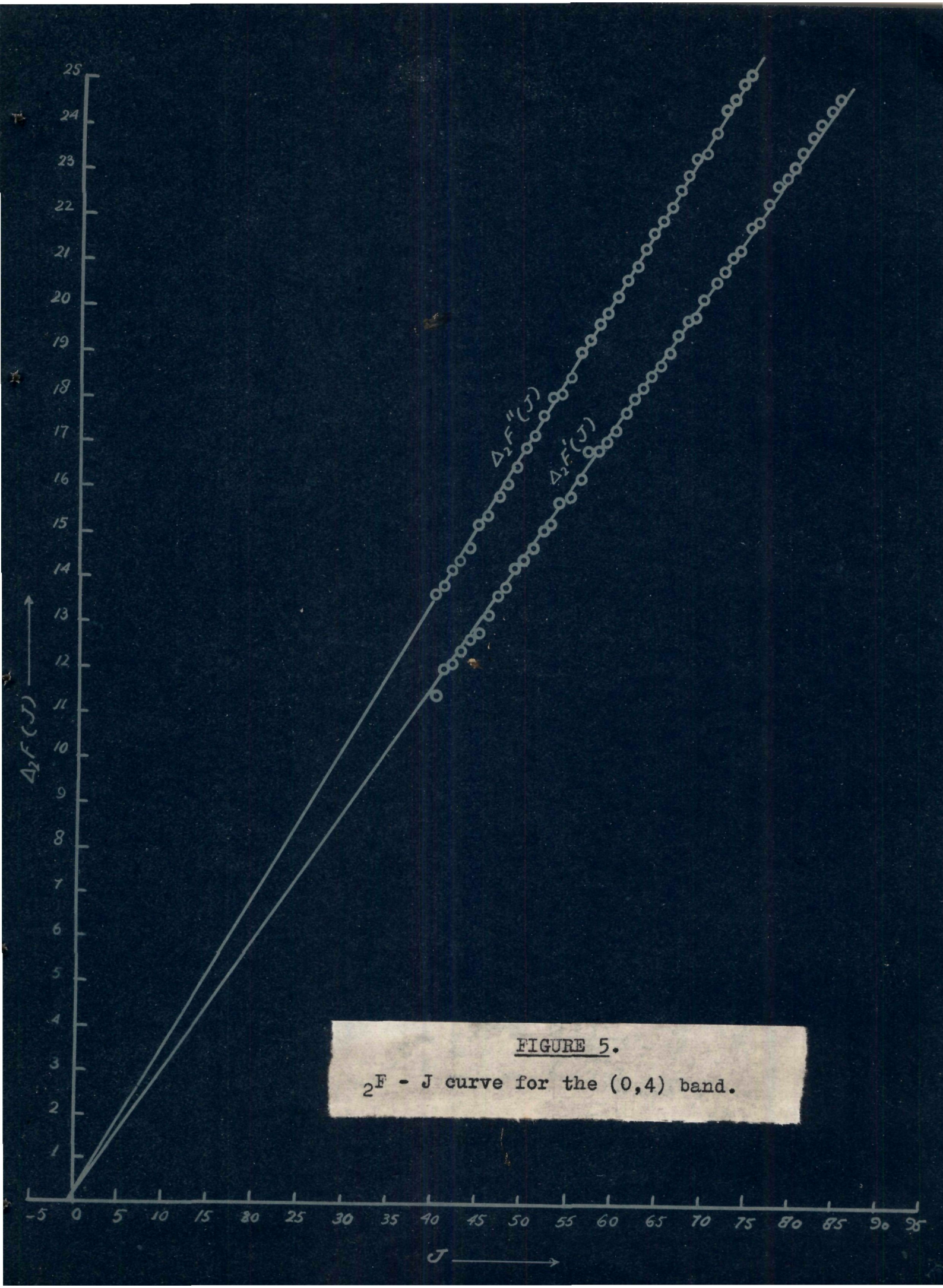

FIGURE 5.

$_2F$ - J curve for the (0,4) band.

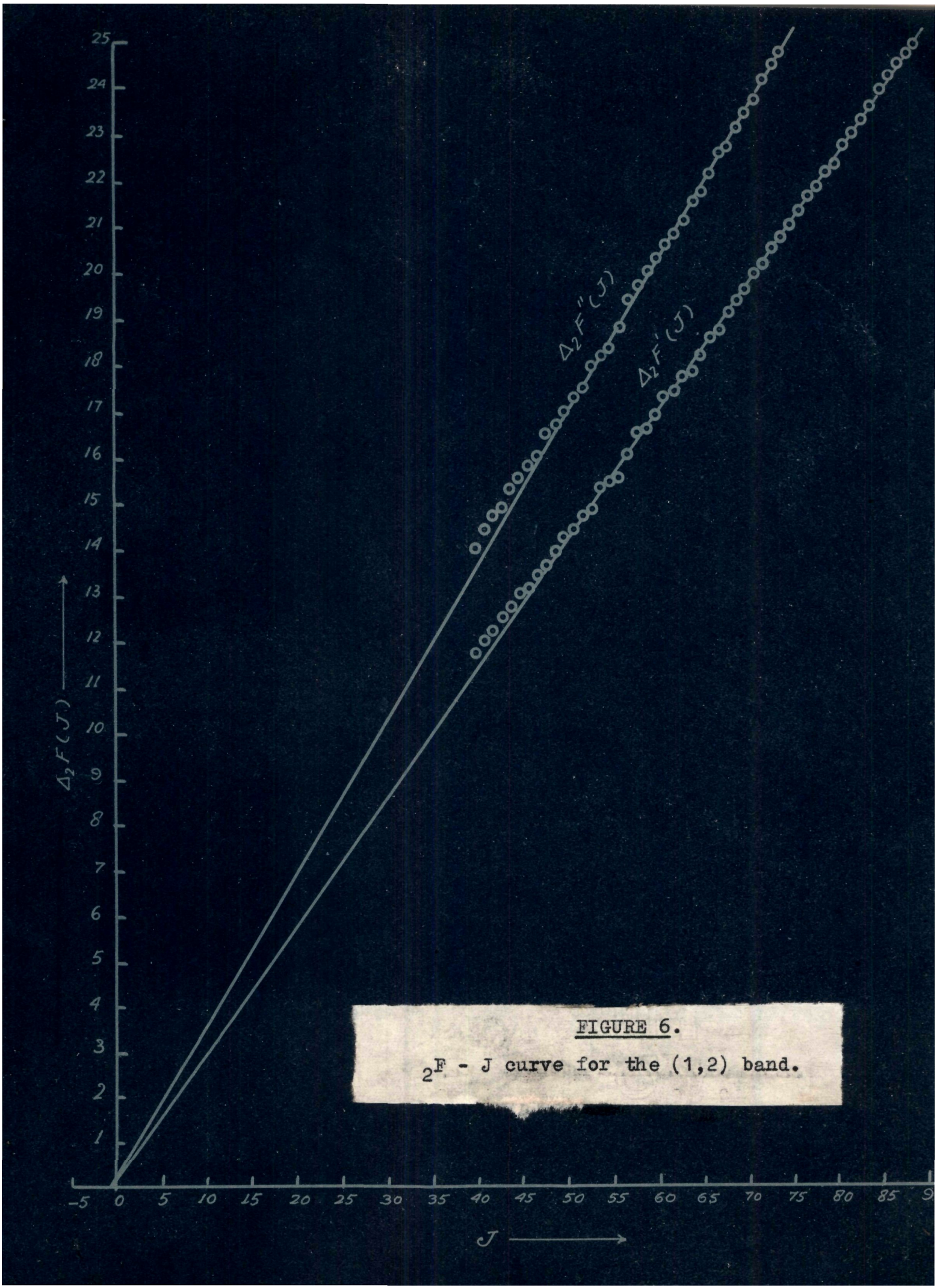

FIGURE 6.

^2F - J curve for the (1,2) band.

Table VI.

The B'_v and B''_v values of the different bands studied.

Band (v', v")	ν_{head} in cm^{-1}	Neglecting D_v		Taking D_v into consideration.	
		B'_v in cm^{-1}	B''_v in cm^{-1}	B'_v in cm^{-1}	B''_v in cm^{-1}
0, 2	21146	0.0717_0	0.0836_9	0.0718_6	0.0837_9
0, 3	20843	0.0713_7	0.0826_6	0.0716_8	0.0830_9
0, 4	20543	0.0716_2	0.0826_5	0.0718_8	0.0827_9
1, 2	21361	0.0699_5	0.0835_6	0.0702_0	0.0839_2

the centrifugal stretching constant is not neglected the expression for $\Delta_2 F$ comes out to be[2]

$$\Delta_2 F(J) = (4B_v - 6D_v)(J + 1/2) - 8D_v(J + 1/2)^3$$

Neglecting $6D_v$ in the first bracket in comparison to $4B_v$,

$$\Delta_2 F(J) = 4B_v(J + 1/2) - 8D_v(J + 1/2)^3$$

As the deviation of the curve $\Delta_2 F(J)$ versus J from a straight line could not be determined with any accuracy, D_v is calculated from the theoretical formula[2]

$$D_v \approx D_e = \frac{4B_e^3}{\omega_e^2}$$

where the value obtained earlier for B_v by neglecting centrifugal stretching constant is used for B_e. The values of $8D_v(J + 1/2)^3$ are then calculated and added to $\Delta_2 F(J)$ after which $\frac{\Delta_2 F(J) + 8D_v(J + 1/2)^3}{J + 1/2}$ is evaluated for different values of J. A mean of this gives probably a more correct value for $4B_v$ than the one obtained earlier by completely neglecting D_v. This procedure has been adopted for all the four bands and the values thus obtained for B_v'' and B_v' are included in table VI. As the upper or lower states are common to the different bands studied, it has been possible to obtain B_v' or B_v'' from measurements of the rotational structure in different bands and are listed as such in table VI; for example B_v' is obtained separately from three different bands (0, 2) , (0, 3) and (0, 4). For such cases mean value is to be taken for getting the final B_v' or B_v''.

The different B_v' and B_v'' values thus obtained can be

finally summarised as

$B'_0 = 0.0718$ cm^{-1} $\quad B'_1 = 0.0702$ cm^{-1}

$B''_2 = 0.0833$ cm^{-1} $\quad B''_3 = 0.0830$ cm^{-1} and $B''_4 = 0.0827$ cm^{-1}

From these values of B'_v and B''_v, the constants B'_e and B''_e as well as α'_e and α''_e are calculated using the relation

$$B_v = B_e - \alpha_e(v + 1/2)$$

and are listed in table VII. The values of I'_e and I''_e as well as r'_e and r''_e are then obtained from the relation

$$B_e = \frac{h}{8\pi^2 c I_e} = \frac{h}{8\pi^2 c \mu r_e^2}$$

and included in table VII.

The difference between the $\nu_{head} - \nu_0$ are calculated from

$$\nu_{head} - \nu_{origin} = -\frac{(B'_v + B''_v)^2}{4(B'_v - B''_v)}$$

for all the different bands and are listed in table VIII. The band origins are only about 0.5 cm^{-1} from the head.

The band origins can be calculated by plotting the combination difference R(J - 1) + P(J) against J^2. The graph is expected to show a stright line because of the relation

$$R(J - 1) + P(J) = 2\nu_0 + 2(B'_v - B''_v) J^2$$

The intercept of the straight line on the ordinate axis gives

Table VII.

The molecular constants* obtained for BiCl.

$B'_e = 0.0726_0$ cm^{-1}	$B''_e = 0.850_9$ cm^{-1}
$\alpha'_e \simeq (0.0016)$ cm^{-1}	$\alpha''_e \simeq (0.0005)$ cm^{-1}
$I'_e = 385.4 \times 10^{-40}$ gm.cm^2	$I''_e = 328.8 \times 10^{-40}$ gm. cm^2
$r'_e = 2.78_4 \times 10^{-8}$ cm	$r''_e = 2.57_3 \times 10^{-8}$ cm

*The values of $h = 6.623_4 \times 10^{-27}$ erg/sec and $c = 2.9977_6 \times 10^{10}$ cm/sec are used in the calculation of the constants.

Table VIII.

The calculated (ν head-ν origin) values for the different bands studied.

Band (v',v")	Band head in cm^{-1}	$B'_v + B''_v$ in cm^{-1}	$B'_v - B''_v$ in cm^{-1}	ν Head-ν origin in cm^{-1}
0, 2	21146	0.1556_5	$-0.0119_{\not 3}$	0.51
0, 3	20843	0.1547_7	-0.0114_1	0.53
0, 4	20543	0.1546_7	-0.0109_1	0.55
1, 2	21361	0.1541_2	-0.0137_2	0.43

$2\nu_0$ while the slope gives $2(B'_\upsilon - B''_\upsilon)$. The band origins obtained in this way are listed in table IXB. As only rotational lines corresponding to high J values are measured, large extrapolations were involved in the determination of the band origins because of which they can not be claimed to have been determined with much accuracy.*

The Electronic Transition Involved.

The fact that the rotational structure of the bands contains only the P and R branches shows that the transition involved is either a $\Sigma - \Sigma$ if Hund's case (a) or (b) type coupling holds good or a $0 - 0$ if Hund's case (C) type coupling holds good. If it is a $\Sigma - \Sigma$ transition, it could be $^1\Sigma - {}^1\Sigma$ transition where only simple P and R branches are expected or it could be a $^n\Sigma - \Sigma$ with higher multiplicity where the expected multiplet structure of the individual lines in the P and R branches is not resolved. We will come back to this point after discussing the different low lying possible electronic states of the BiCl molecule.

The two atoms that form the BiCl molecule belong to different periods of the periodic table and thus have

Table IX.B

Band origins obtained from the graph.

Band v', v''	ν_{head} in cm^{-1}	ν_{origin} in cm^{-1}	From graph $B_{v'} - B_{v''}$	From table VIII. $B_{v'} - B_{v''}$
0,2	21146	21145.5	-0.01185	-0.01193
0,3	20843	20842.7	-0.01120	-0.01141
0,4	20543	20542.7	-0.01094	-0.01091
1,2	21361	21355.5	-0.01433	-0.01372

very different nuclear charge. In such a case the closed shells of the separated atoms need not be taken into account while assigning an electronic configuration to the molecule. It is sufficient for practical purposes to consider the electrons outside the filled shells. The lowest electronic configuration for the two atoms in the present case are as follows:

$$Bi \text{ ——— } (KLMNO_{spd})\ 6s^2 6p^3$$

$$Cl \text{ ——— } (KL)\ 3s^2 3p^5$$

Following Mulliken's[3] notation the lowest electronic configuration for the BiCl molecule may be then written as

$$(KKLLMNO_{spd})(_3\sigma)^2(_4\sigma)^2(\chi\sigma)^2(\omega\pi)^4(\upsilon\pi)^2$$

where $_3\sigma$ and $_4\sigma$ represent respectively the bonding and antibonding orbital of the type $(6s\sigma_{Bi} + 3s\sigma_{Cl}, \sigma)$ and $(6s\sigma_{Bi} - 3s\sigma_{Cl}, \sigma)$, $\chi\sigma$ represents the bonding orbital of the type $(6p\sigma_{Bi} + 3p\sigma_{Cl}, \sigma)$ and $(\omega\pi)$ and $(\upsilon\pi)$ represent respectively the bonding and antibonding electrons of the type $(6p\pi_{Bi} + 3p\pi_{Cl}, \pi)$ and $(6p\pi_{Bi} - 3p\pi_{Cl}, \pi)$. This configuration gives the electronic terms $^3\Sigma^-(0^+,1)$ $^1\Delta(2)$ and $^1\Sigma^+(0^+)$ of which $^3\Sigma^-(0^+,1)$ is expected to lie lowest according to Hund's rule. Thus $^3\Sigma^-(0^+,1)$ appears to be very pro-

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O_{spd} means O shell in which only the sub groups s, p, d are filled up.

The terms in the bracket are the Hund's case (c) analogues of the terms outside the brackets. Thus for example 0^+ and 1 are the case (c) analogue of the $^3\Sigma^-$ term of the Hund's case (a) or (b) type coupling.

bably the ground state of the BiCl molecule. The ground state of the molecule as pointed out in the earlier chapter is also very likely the lower state of the band system 6170 - 4220A as this system has been obtained by Morgan earlier in absorption.

The examination of the probable terms from the approach of the separated atoms will throw additional light on the problem. The ground state of the molecule is expected to dissociate into Bi($^4S_{3/2}$) and Cl($^2P_{3/2}$) which represent respectively the ground states of the Bi and Cl atoms. The electronic terms that can be derived from Bi($^4S_{3/2}$) + Cl($^2P_{3/2}$) atoms are $^3\Sigma^-$(0^+,1), $^3\Pi$ (2,1,0^+,0^-), $^5\Sigma^-$(2,1,0^-) and $^5\Pi$ (3,2,1,1,0^+,0^-). A consideration of the problem from the approach of the united atom will help us to find out which of these ~~five~~ four states are low lying states. The electronic terms of the BiCl molecule are expected to be quite similar to those of the NF molecule as Bi and Cl respectively belong to the same groups of the periodic table as N and F. Nitrogen has seven electrons with the configuration $1s^2 2s^2 2p^3$ and Fluorine has nine electrons with the configuration $1s^2 2s^2 2p^5$. The molecule NF can be supposed to have been formed by splitting the united atoms sulphur which has sixteen electrons. The electronic terms of the molecule that result by splitting the sulphur atom in its low lying $^3P_{2,1,0}$ states are $^3\Sigma^-(0^+,1)$ and $^3\Pi$ (2,1,0^+,0^-). These two states are expected to lie lowest of all the electronic states of the N,F molecule and therefore also of the

BiCl molecule.

Of the four different states $^3\Sigma^-(0^+,1)$, $^3\Pi(2,1,0^+,0^-)$ $^5\Sigma^-(2,1,0^-)$ and $^5\Pi(3,2,1,1,0^+,0^-)$ that are derived from the separated atoms Bi(^4S)+Cl(^2P) only $^3\Sigma^-(0^+,1)$ and only $^3\Pi(2,1,0^+,0^-)$ can be expected to be stable as they can be correlated to the corresponding lowest states derived from the united atom approach. The $^5\Sigma^-(2,1,0^-)$ and $^5\Pi(3,2,1,1,0^+,0^-)$ are higher and are probably repulsive as they can not be derived from the low lying ^3P, ^1S or ^1D states of the united atom and can be derived only from very high ~~low~~ excited states of the united atom.

Thus considering the correlation of the separted and united atom approaches, it is clear that the $^3\Sigma^-(0^+,1)$ and $^3\Pi(2,1,0^-,0^+)$ are the low lying states of BiCl molecule and that they dissociate into Bi(^4S)+ Cl(^2P) atoms. Of these $^3\Sigma^-(0^+,1)$ is to be correlated with the $^3\Sigma^-(0^+,1)$ which arises from the lowest electronic configuration $(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4(2\pi)$ and which or a component of which is the ground state of the molecule and also probably the lowest state of the system 6170-4220A. The other two terms $^1\Sigma^+(0^+)$ and $^1\Delta(2)$ that are derivable from the same configuration can not dissociate in-

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It may be mentioned that the conclusion that $^3\Sigma^-$ and $^3\Pi$ lies lower than $^5\Sigma^-$ and $^5\Pi$ states is in agreement with what one expects from the generalization of the Heitler - London Theory for complicated cases.

to Bi(^4S) + Cl(^2P) atoms and go to higher dissociation products.

As the upper state of the band system 6170-4220Å is supposed to dissociate into Bi($^4S_{3/2}$) + Cl($^2P_{1/2}$) atoms, the above considerations show that $^3\Pi$ (2,1,0$^+$,0$^-$) or its components probably represents the upper state. The lowest configuration that yields a $^3\Pi$ (2,1,0$^+$,0$^-$) state is $(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\pi)^4(7\pi)(8\sigma)$ where 8σ represents an anti bonding orbital of the type $(6p\sigma_{Bi}-3p\sigma_{Cl})$ and other symbols are as explained earlier.

Now we should correlate these results with the experimental observations. The study of the rotational structure shows only P and R branches from which it was clear that the transition involved has to be a $\Sigma - \Sigma$ if Hund's case (a) or (b) type coupling takes place in the molecule or a 0 — 0 if Hund's case (c) type coupling takes place. The transition can not be a $^1\Sigma - ^1\Sigma$ transition as there is no $^1\Sigma$ state derivable from the normal Bi(^{4}s) + Cl(^{2}P) atoms. It can not be also a $\Sigma - \Sigma$ involving a higher multiplicity as there are no two stable Σ states that arise from the normal Bi(^{4}s) + Cl(^{2}P) atoms. This means that the transition can not be any $\Sigma - \Sigma$ transition and therefore the coupling involved is not Hund's cas (a) or (b) type.

Thus it is clear that the transition involved is probably a 0— 0 transition where the coupling is of Hund's case (c) type. The transition appears to be very probably

$(3\sigma)^2\ (4\sigma)^2(x\sigma)^2\ (\omega\pi)^4\ (v\pi)^2\ {}^3\Sigma^-(0^+)$ ←——

$(3\sigma)^2(4\sigma)^2\ (x\sigma)^2(\omega\pi)^4(v\pi)^1(u\sigma)^1\ {}^3\pi(0^+)$

The transition is not a case (a) or (b) type transition but a case (c) type ${}^3\Sigma^-(0^+)$ — ${}^3\pi(0^+)$ transition which can also be written as 0^+ — 0^+.

As examples of the band system in which Hund's case (c) type coupling takes place one may point out the ${}^1\Sigma^+(0^+)$ — ${}^3\pi(0^+)$ transition of the visible absorption bands of halogens[2,4,5] which show only P and R branches. The other examples are $Bi^{209}H'$ and $Bi^{209}H^2$ where the rotational structure reveals (0-1 and 0-0) and (0-0) transitions respectively.[6,7]

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CHAPTER V.

Emission spectrum of Bismuth Monobromide molecule.

The Emission Spectrum of BiBr molecule

Abstract.

Bismuth bribromide vapour was excited by a condensed transformer discharge and a band system was obtained in the region 5780 — 4650 A. About 240 as many as 60 bands were measured in four spectrograms of which about 68 bands were obtained in absorption. The vibrational constants obtained by Morgan were found to satisfy all the bands obtained in the present investigation after the addition of a double term for the upper as well as lower states were found to be necessary to join the ground state dissociation limit. The dissociation energies of the upper and lower states were found to be 18427 cm^{-1}, and 22120 cm^{-1}. This system lies between 6170 - 4220 A and is of the type of which the electronic transition involved is probably $(3\sigma)^2(4\sigma)^2(2\sigma)^2(\omega\pi)^4(\upsilon\pi)(4\sigma)\,{}^3\Pi(0^+) \longrightarrow (3\sigma)^2(4\sigma)^2(2\sigma)^2(\omega\pi)^4(\upsilon\pi)^2\,{}^3\Sigma^-(0^+)$.

Introduction.

Morgan[1] studied the absorption spectrum of bismuth monobromide by passing bromine vapour over molten mass of bismuth placed in an open tube which in turn was surrounded by a furnace which was heated upto about 900°C. Two systems, one in the region 5433 - 4504A and the other in the region 4130 - 3360A were observed and analysed. On the basis of the vibrational analysis that was supported by the observed-isotopic shifts, these two band systems were attributed to the BiBr molecule. The earlier two chapters dealt with the emission spectrum of BiCl molecule, where a number of new results obtained were discussed. The present chapter deals with the emission spectrum of BiBr molecule and the corresponding vibrational analysis and discussion.

There is a reference in the Science Abstracts (Abstract No. 2566, Vol. 38, 1935) concerning a paper entitled "New Band Spectra" by H. G. Howell and G. D. Rochester, Univ. Durham, Phil. Soc. Proc. 2, pp. 123-24, Dec. 1934. It is reported that the observed spectra of 3 different molecules are briefly described, of which BiBr is one. It appears from the abstract that the wavelength data and analysis of the different systems of PbS only are given in the paper, and that the wavelength data and the analysis of BiBr bands are not given. Morgan also stating about this reference that "Howell and Rochester using a high frequency electrical discharge have produced emission band spectra of BiBr and BiI, but no analysis of the observed systems seems to have been made". This journal, unfortunately, is not become available to me though attempts are made in three different Universities. Attempts are being made to get a photo copy of the necessary paper in the journal so that the experimental data, if any concerning the wavelengths of the band heads, can be compared with the present

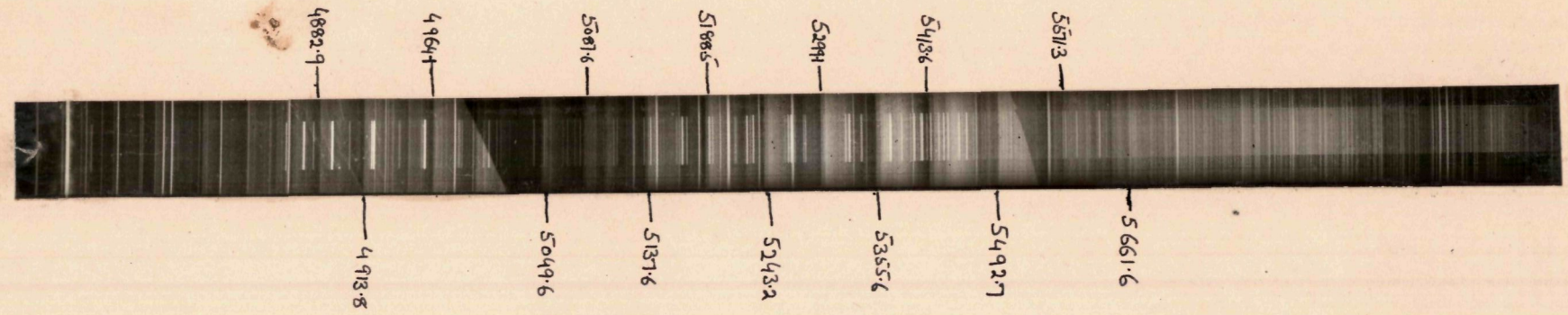
EXPERIMENTAL DETAILS.

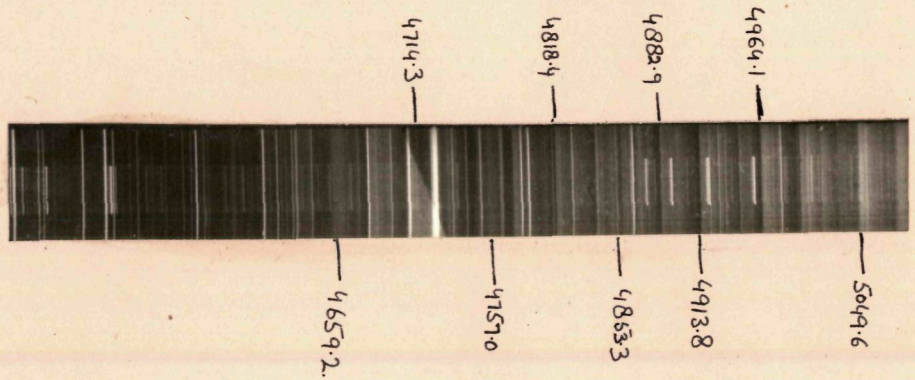
The vapour of bismuth tribromide was excited by means of an uncondensed transformer discharge. The discharge tube was made of pyrex glass and was 40 cms in length and 0.6 cms in diameter. Cylinderical nickel electrodes placed coaxially along the length of the discharge tube were found suitable for exciting the molecule. The dehydrated sample of bismuth tribromide obtained from E.Merck was introduced inside the discharge tube at one end near one of the electrodes. The other end of the discharge tube was connected to a rotary pump through a side tube and was continuously evacuated during the experiments. The sample was heated intermittently by a Bunsen burner so as to regulate the flow of the vapour through the discharge tube such that the colour of the discharge was intense bluish green. During the preliminary experiments, it was experienced that if the sample was overheated, the colour of the discharge turns brownish, which might, probably, be due to the decomposition of bromide into atomic bromine and bismuth.

Only one system lying in the region 5714 - 4651A was observed. About 200 bands of this system were recorded in the present emission spectrum as against 60 bands recorded by Morgan in his absorption experiments. The second band system in the region 4130 - 3860A observed in absorption by Morgan was not detected.

FIGURE I.

The enlargement of the 5710-4650A system of BiBr taken on the three prism glass spectrograph.





The spectrum was first photographed on the Hilger Medium Quartz spectrograph and then on the three prism glass Zeiss spectrograph which is having a dispersion of 11.4A°/m.m. at 4800A; Fig. I shows the enlargement of the spectrum as obtained from the three prism glass spectrograph. The bands in general are degraded towards longer wavelengths, the measurements of which were made with an Abbe comparator. The error involved in the measurements of the band heads is estimated to be not more than ± 4 cm^{-1}.

Vibrational Analysis.

The wavelengths, wavenumbers and their visually estimated relative intensities, are given in Table I. The bands observed in absorption by Morgan are also included in the table for comparison. Table II gives the vibrational analysis of the band system in the region 5714 - 4651A and the corresponding intensity distribution is given in Table III. All the bands could be fairly well represented by the formula

$$\nu = 20494.6 + (134.1v' - 0.674v'^2 - 0.1002v'^3) - (207.1v'' - 0.458v''^2 - 0.00073v''^3) \quad \ldots\ldots\ldots (1)$$

in which the constants for the upper and lower states are the same as reported by Morgan with the exception that an additional cubic term has been added in the equation for the ground state.

Table I

Morgan's absorption ν_{vac}	Present experiments (electrical excitation of BiBr) λ_{air}	I	ν_{vac}	v' & v"	$(\nu_0 - \nu_c)$
	5713.7	1	17497	(10,21)*	-1
	10.1	1	17508	(10,22),(16,23)*	3, -1
	04.2	3	17526	(10,21)	0
	5698.0	0	17545	(13,29)*	0
	95.1	2	17554	(13,23)*	0
	90.0	2	17570	(13,22),(7,19)*	-5, -4
	83.1	4	17591	(9,20)*,(11,21)*	-1, 6
	74.1	2	17619	(9,20)	0
	69.3	2	17634	(14,22)	-2
	66.7	3	17642		
	61.6	3	17658	(0,14)*,(12,21)*, (15,22)*	-3, -5, 2
	52.0	2	17685	(15,22),(9,19)*,(10,20)*	-2, 4, -2
	43.4	6	17715	(10,20)	2
	39.5	6	17727	(5,17)*,(17,22)*,(13,21)*	2, 3, 2
	37.1	1	17735	~~(9,15)*~~ (13,21)*, (2,15)*	2 2,3
	34.3	6	17742	(10,22)*	1
	31.6	6	17752	(5,17)	2
	27.2	2	17764	(13,21),(7,19)*	2, -1
	20.2	3	17783	(7,19),(14,21)*,(9,19)*, (4,15)*	-1, -5, 5, -7
	15.2	0	17792	(11,20)	2
	11.4	4	17816	(4,15)	-2
	05.7	0	17824		
	5699.2	5	17838	(0,13)*,(12,20)*,(3,15)*	-1, 4, -7

N.B: The assignments marked (*) correspond to the $Br^{79}Br^{81}$ molecule, while the rest correspond to $Br^{81}Br^{81}$ molecule.

Table I (continued)

Forbidden absorption ν_{obs}	λ (Å)	I	ν_{calc}	J' ; J"	$\nu_{obs} - \nu_{calc}$
55[illegible]	[illegible]	4	17[illegible]	(3,15),(11,23),(15,21)†; (13,1)†	-3, 4, -1, 1
59.[illegible]	[illegible]	1	17[illegible]	(13,13)	1
70.7	[illegible]	1	17[illegible]7	(5,17)†,(17,21)†	-1. 3
70.1	[illegible]	1	17[illegible]	(11.23)†,(3,11)†	0, -3
71.[illegible]	[illegible]	1	17[illegible]	(3,15)	3
72.[illegible]	[illegible]	1	17[illegible]7	(3,11), (13,[illegible])	-3
64.2	[illegible]	2	17[illegible]	(1,11)*,(11,13)*	-6. 3
59.9	[illegible]	5	17[illegible]	(7,17),(11,19)*	1, -1
57.7	[illegible]	3	17[illegible]	(11,21),(1,15),(1,13)*	-1, -1, -3
41.7	[illegible]	2	17[illegible]	(5,19)*,(11,13)*	5, -3
35.[illegible]	[illegible]	2	17[illegible]	(1,19),(3,17)*(3,1)*	-1, 3, -1
29.7	[illegible]	3	17[illegible]	(13,13),(15,23),(1,17)* (13,1)*	-1, 1, 1, -1
13.1	[illegible]	2	17[illegible]	(3,14)	1
[illegible]1.7	[illegible]	[illegible]	17[illegible]	(17,23)*	1
12.3	[illegible]	2	17[illegible]	(11,13)*,(13,13)*	3, 1
11.[illegible]	[illegible]	2	17[illegible]	(1,13)*	-1
10.3	[illegible]	2	17[illegible]	(3,13)	3
11.[illegible]	[illegible]	1	17[illegible]	(13,13)	1
10.[illegible]	[illegible]	1	17[illegible]	(1,13)	-1
[illegible].3	[illegible]	1	17[illegible]	(7,13)*,(11,17)*	5, -1
01.3	[illegible]	1	17[illegible]	(1,17)*	-1
01.7	[illegible]	1	17[illegible]	(7,15)	3
[illegible]0.3	[illegible]	2	17[illegible]	(11,17),(11,19)	-1, 1

Table 5 (continued)

ν_{obs}	λ_{obs}	ν_{calc}	J', J''	$\nu_{obs}-\nu_{calc}$
	5477.0	18256	(3,17),(1,18),(4,18)	-2, -2, 3
	5481.6	18241		
	5487.7	18221	(1,18)	1
	5488.6	18218	(1,18), (1,18)	-1, 2
	5491.2	18211		
	5491.7	18210	(1,18), (3,15)	1, 0
	5492.3	18208	(5,18),(15,18),(0,18), (1,18)	-2, -2, -1, -1
	5493.1	18205	(8,18), (3,18)	-1, -1
	5494.0	18202	(3,18)	-1
	5494.4	18201	(18,18)	1
	5496.7	18193	(3,18)*,(18,18)*	-2, 2
	5497.1	18191		
	5501.0	18178	(3,18), (7,15)*	0, -2
	5502.0	18174	(3,18)*	-1
	5503.6	18170	(7,15),(11,17),(14,18)*	1, -2, 1
	5504.4	18167	(3,18), (4,18)*	-2, -1
18305.6	5505.0	18165	(18,18), (1,18)*	-4, -2
	5506.2	18162		
18161.6	5507.7	18157	(1,18), (4,18)	-3, 3
	5508.6	18154	(6,18)*, (12,17)*	0, 1
	5509.0	18153	(15,18)	-1
18150.2	5510.1	18149	(3,18),(12,17),(9,18)*, (3,18)*,(3,15)*	3, 1, -3, -3, -3

Table I (continued)

Morgan's absorption	Present experiment (electrical excitation of DIm)				
ν_{vac}	λ_{air}	I	ν_{vac}	v', v"	$(\nu_0 - \nu_{obs})$
18460.2	13.6	(7)	18467	(0,10),(13,12),(8,15)	-2, -2, -4
	5393.4	0	18519	(5,13),(13,17),(2,11)*	-2, 1, 0
	22.2	0	18540	(2,11),(11,16)*,(7,14)	3, 0, 1
	28.2	1	18571	(9,15)	-1
	5381.5	2	18577	(4,12)*	-1
18585.0	5379.3	2	18583	(1,10)	-2
	75.1	2	18599	(4,12)	4
18603.4	74.6	2	18601	(1,10)	-1
	70.5	2	18615	(12,16)*	-1
	67.4	2	18626	(15,17), (6,13)*	-4, 4
18652.2	60.4	10	18650	(0,9)*, (3,11)*	0, 1
18668.1	55.6	8	18667	(0,9),(3,11),(10,15)	0, 2, 1
	40.1	0	18721	(5,13), (2,10)*	4, 3
	37.0	0	18732	(2,10)	-2
	28.7	1	18761	(9,14)	-4
18786.3	22.2	2	18784	(1,9)*	-1
802.2	18.2	3	18798	(1,9)	-3
852.6	03.6	9	18850	(0,8)*,(3,10)*	-2, 2
867.5	5299.1	7	18866	(0,8), (3,10)	-1, 3
	91.5	2	18893	(17,16), (5,11)	0, -5
	88.4	1	18904		
18917.4	81.7	0	18923	(2,9)	-4
	66.4	0	18983	(1,8)*	-3
	63.9	0	18992	(4,10)	4

Table I (continued)

Morgan's absorption	Present experiment (electrical excitation of BiBr)				
ν_{vac}	λ_{air}	I	ν_{vac}	v' , v"	$(\nu_0 - \nu_c)$
	5260.9	1	19003	(1,8)	3
	57.0	2	19017	(15,15), (6,11)*	3, 0
	48.6	3	19047	(3,9)*	-1
19054.6	47.1	8	19053	(0,7)*	-1
	45.1	7	19060	(3,9)	-1
19067.9	43.2	6	19067	(0,7)	0
	29.5	3	19117	(2,8)*	-2
	26.8	3	19127	(2,8)	-4
	15.3	1	19169	(4,9)	-6
	11.5	1	19183	(4,9), (1,7)*	-4, -5
	05.8	19204		(1,7)	4
	51944.4	5	19246	(3,8)*	-3
19257.6	91.7	6	19256	(3,8), (0,6)*	-4, -1
268.6	88.5	19268		(0,6)	0
320.9	74.5	3	19320	(2,7)*	-1
193305	5170.8	1	19334	(2,7)	2
	58.5	2	19380	(4,8)*	4
	56.1	0	19389	(1,6)*	-2
	53.5	0	19399	(1,6)	-2
	50.5	0	19410	(12,12)	-4
	48.4	?	19418	(6,9)*	2
19461.4	37.6	19459		(3,7), (0.5)*	-1, -2
470.5	34.9	4	19469	(0,5)	-1
	31.3	2	19481	(13,12)	-4
	30.5	0	19486		

Table I (continued)

Morgan's absorption	Present experiment (electrical excitation of BiBr)				
ν vac	λ air	I	ν vac	v', v"	($\nu_0 - \nu_c$)
	26.5	?	19501		
	20.7	1	19523	(2,6)*	-1
	18.6	2	19531	(2,6), (7.9)	-2, 2
	13.4	1	19551	(9,10)*	3
	10.3	0	19563		
	08.7	0	19569		
	04.5	2	19585	(4,7)	-1
19596.3	02.4	4	19593	(1.5)*	-2
604.6	00.6	3	19600	(1,5)	-3
	5094.4	?	19624		
	92.0	19633		(3,9)*	-4
	87.6	4	19650	(3,9), (3,6)*	4, -4
	85.1	3	19660	(3,6)	-1
19666.8	83.8	3	19665	(0,4)*	-1
674.5	81.7	3	19673	(0,4)	0
	74.5	1	19701	(5,7)*	1
	70.9	0	19715	(11,10)*	-4
	68.6	1	19724	(11,10),(2,5)*,(~~7,8~~)*	-4,-4, *
	66.8	1	19731	(7,8)*	1
	65.0	1	19738	(2,5),(7.8),(9,9)*	3, 0, 0
	51.9	1	19789	(4,6)	2
19801.3	49.6	5	19798	(1,4)*	-2
	47.3	3	19805	(1,4)	-2
	38.9	1	19840	(3,8), (10,9)	5, -1
	5034.6	0	19857	(3,5)*	0

Table I (continued)

Morgan's absorption ν vac	Present experiment (electrical excitation of BiBr) λair	I	ν vac	v' , v"	$(\nu_0 - \nu_c)$
	50 32.6	0	19865	(3,5), (0,3)*	2 , -6
	29.5	3	19877	(0,3)	0
	18.7	1	19920	(11,9)*	1
19932.7	14.9	3	19935	(2,4), (7,7)	-3, -3
37.6	13.4	0	19941	(9,8)	-5
	08.9	0	19959		
	02.7	3	19984	(4,5)	-4
20007.6	4997.4	5	20005	(1,3)*	-1
012.6	96.1	3	20010	(1,3)	-1
	91.9	0	20027	(6,6)	1
	90.0	0	20034	(10,8)*, (8,7)*	1, -6
	82.5	0	20065	(3,4),(13,9)*	-2, -3
079.1	77.5	0	20085	(0,2)	3
	73.2	2	20102	(5,5)*	1
	69.8	3	20116	(5,5), (11,13)*	-1, -4
	67.3	0	20126	(11,8)	-1
20140.0	64.1	5	20139	(2,3),(7,6),(9,7)*	-2, 0, -2
143.4	61,4	?	20150	(9,7)	4
	59.4	1	20158		
	57.7	0	20165		
	55.0	2	20176		
	51.3	0	20189	(4,4)	-3
	49.6	0	20198	(12,8)*	-1
20215.5	45.7	4	20214	(1,2)	-1
	42.5	0	20227	(6,5)	-2
	41.3	0	20232	(10,7)*	-3

Table I (continued)

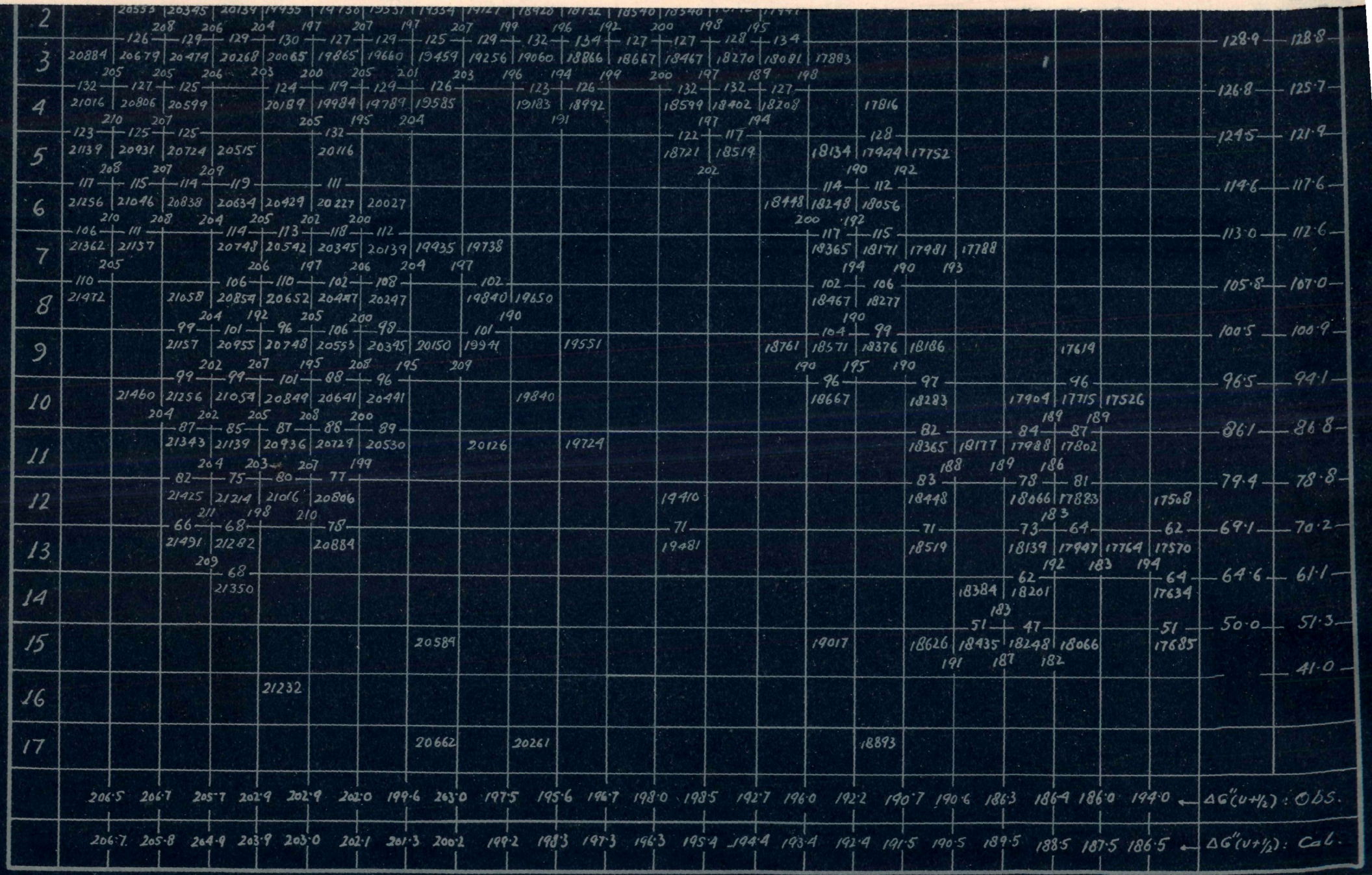
Morgan's absorption.	Present experiment (electrical excitation of BiBr)				
ν vac	λ air	I	ν vac	v' , v"	$\nu_0 - \nu_c$)
	4937.6	0	20247	(3,6)	1
	34.2	3	20261	(17,9)	1
20268.8	32.5	0	20268	(3,3), (13,8)*	-3, 0
	26.7	0	20292	(0,1), (0.1)*	4, 6
347.8	13.8	5	20345	(2,2),(7.5),(9,6), (7,5)*	-2, 4, -2, 6
	08.?	1	20366		
	4895.3	2	20422	(1,1)	1
	93.6	2	20429	(6,4)	-3
	4890.8	2	20441	(10,6)	0
	89.3	0	20447	(3,5)	-1
	84.8	2	20466	(13,7)*	4
20476.7	82.9	5	20474	(3,2)	-1
	78.1	0	20494	(0,0)	-1
	76.0	0	20503		
	73.1	1	20515	(5,3)	-3
	69.6	0	20530	(11,6), (14,7)*	2, -1
	66.7	3	20542	(7,4)	-3
20553.3	64.1	3	20553	(2,1), (9,5)	0, 2
	56.8	3	20584	(15,7)	-4
20600.9	53.3	4	20599	(4,2), (12,6)*	-2, -4
	48.8	3	20618		
	46.4	0	20623	(1,0)	0
	45.0	2	20634	(6,3)	-2

Table I (continued)

Morgan's absorption	Present experiment (electrical excitation of BiBr)				
ν vac.	λ air	I	ν vac	v', v"	$(\nu_0 - \nu_c)$
	43.4	0	20641	(10,5)	-2
	40.8	2	20652	(3,4)	1
	38.5	2	20662	(17,7)	3
	36.6	2	20670	(13,6)*	-3
206833	34.5	2	20679	(3,1)	-2
	24.0	0	20724	(5,2), (11,5)*	1 , -6
	22.9	0	20729	(11,5),(14,6)*	-1, -5
	18,4	2	20748	(7,3), (9,4)	0, -4
20809.9	05.0	4	20806	(4,1),(12,5),(4,1)*	-1, -3, -3
	00.3	1	20826		
	4797.6	2	20833	(6,2)	-3
	93.3	0	20854	(8,3), ~~(8,3)~~*	-2, -3
	95.1	0	20849	(10,4)	-2
	87.0	0	20884	(3,0), (13,5)	-4 , 4
20930.8	76.3	3	20931	(5,1)	2
	75.1	4	20936	(11,4),(5,1)*,(14,5)*,	3, 4, -2,
	70.7	0	20955	(9,3)	-1
	69.4	0	20961	(7,2)*, (9,3)*	0, 5, 3
21018.3	57.0	2	21016	(4,0), (12,4)	2, 4
015.9					
047.6	50.2	0	21046	(6,1)	-2
	48.4	0	21054	(10,3), (6,1)*	3, 2
	47.4	0	21058	(8,2)	-2
21135.7	4743.9	1	21074		
21140.7	29.3	2	21133	(5,0), (11,3)	3, 2

Table I (continued)

Morgan's absorption	Present experiment (electrical excitation of BiBr)				
ν vac.	λ air	I	ν vac	v', v"	$(\nu_0 - \nu_c)$
	4726.1	2	21153		
21163.1	25.2	2	21157	(7,1), (9,2)	-3, -4
	14.3	3	21206		
	12.6	3	21214	(12,3)	-2
	09.9	2	21226		
21254.1	07.6	2	21232	(16,4)	-4
21258.0	03.2	0	21256	(6,0), (10,2)	3 , 1
	4697.5	1	21282	(13,3)	-4
	95,7	?	21290	(13,3)*	2
	94.4	1	21296		
	88.5	0	21323		
	84.1	3	21343	(11,2)	1
	82.5	2	21350	(14,3), (11,2)*	3, 4
21365.7	80.0	1	21362	(7,0)	-4
21372.5	76.3	1	21376	(7,0)*, (9,1)*	3, 2
	66.1	0	21425	(12,2)	4
	63.7	0	21436		
	60.5	2	21451		
	~~59.2~~	~~3~~	~~21457~~		
	58.5	3	21460	(10,1)	-2
21473.1	55.9	1	21472	(8,0), (10,1)*	-1, 4
21480.1	54.8	1	21477	(8,0)*	-3
	53.3	1	21484		
	51.8	1	21491	(13,2)	0
	50.9	1	21495	(13,2)*	0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206·5 206·7 205·7 202·9 202·9 202·0 199·6 203·0 197·5 195·6 196·7 198·0 198·5 192·7 196·0 192·2 190·7 190·6 186·3 186·4 186·0 194·0 ← ΔG"(v+½): Obs.
206·7 205·8 204·9 203·9 203·0 202·1 201·3 200·2 199·2 198·3 197·3 196·3 195·4 194·4 193·4 192·4 191·5 190·5 189·5 188·5 187·5 186·5 ← ΔG"(v+½): Cal.

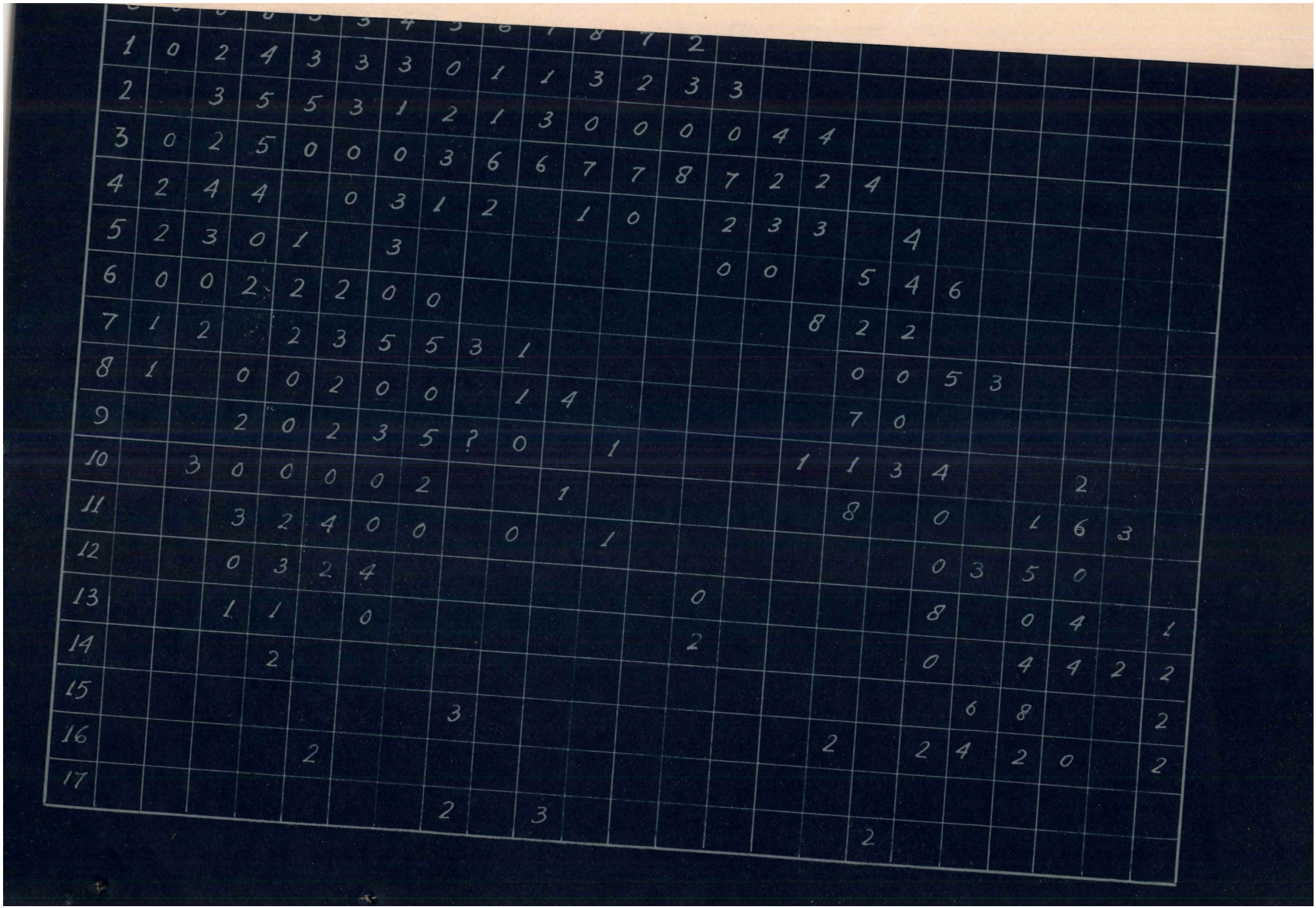
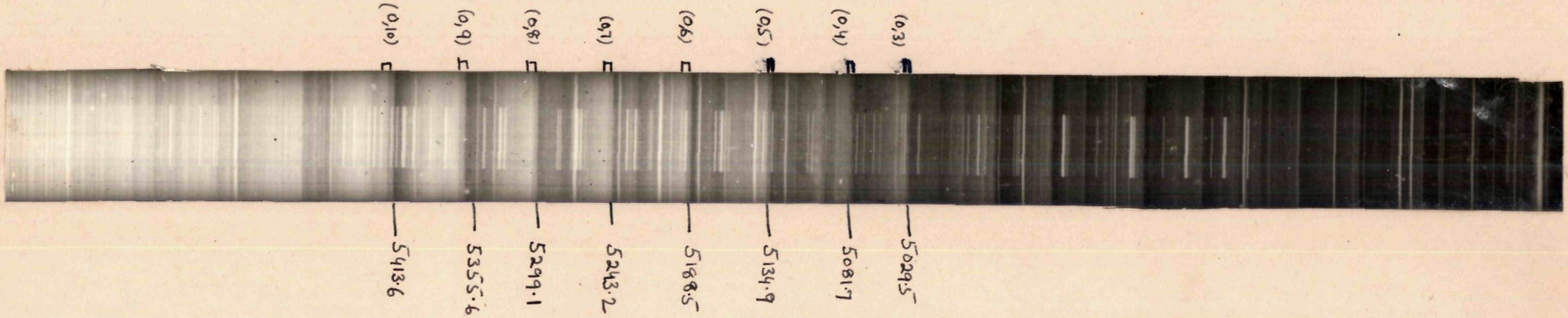


FIGURE II.

Extra enlargement of part of the 5710-4100 A system of BiBr showing some probable isotopic shifts.



Isotopic Shifts.

There are two isotopic species $BiBr^{81}$ and $BiBr^{79}$ for the bismuth monobromide molecule. As the abundance ratio of these isotopic molecules is essentially the same, we expect two isotopic band heads of equal intensities in the present case. It has been possible to identify the isotopic heads for most of the strong bands. Fig II shows someof the strong isotopic band heads observed in the BiBr molecule. The calculated and observed isotopic shifts along with the relative intensities are given in table IV assuming that the vibrational analysis shown in table II corresponds to the $BiBr^{81}$ molecule. The agreement between the calculated and the observed isotopic shifts is fairly good. Table V shows the vibrational analysis representing the $BiBr^{79}$ molecule and table VI the corresponding intensity distribution. It is to be noted that a number of bands are common to the tables II and V, that is a number of bands belonging to $BiBr^{79}$ can also be represented as those belonging to $BiBr^{81}$ with different v', v" values.

The agreement between the observed and calculated isotopic shifts from the present experiments as well as that observed in absorption by Morgan indicated clearly that the band sistem belongs very likely to the BiBr molecule.

The Dissociation Products and The Dissociation energies Of The States Involved.

Since the present band system occurs in emission

Table IV.

Isotopic Band Heads for BiBr.

v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
10, 21	17497 17526	1 3	29	28
13, 22	17545 17570	0 2	25	30
19, 20	17591 17619	4 2	28	27
15, 22	17658 17685	3 2	27	32
10, 20	17685 17715	2 6	30	27
5 , 17	17727 17752	6 6	25	25
13, 21	17735 17764	1 2	29	29
7 , 18	17764 17788	2 3	24	25
4 , 16	17788 17816	3 4	28	24
3 , 15	17856 17883	5 4	27	23
12, 20	17856 17883	5 4	27	27
10, 19	17883 17904	4 1	25	21
5 , 16	17917 17944	4 4	27	23
2 , 14	17922 17947	4 4	25	23
13, 20	17922 17947	4 4	25	27
11, 19	17967 17988	3 5	21	25

v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
6 , 16	18040 18056	2 2	16	22
12, 19	18040 18066	2 0	26	25
3 , 14	18056 18081	2 2	25	22
17, 20	18102 18134	2 5	32	31
5 , 15	18114 18134	3 5	20	21
13, 19	18114 18139	3 4	25	26
2 , 13	18122 18142	3 4	20	21
7 , 16	18154 18171	1 0	17	21
11, 18	18154 18177	1 3	23	23
14, 19	18177 18201	3 8	24	26
1 , 12	18186 18208	4 3	22	22
4 , 14	18186 18208	4 3	22	21
9 , 17	18161 18186	6 4	25	22
0 , 11	18248 18270	2 2	22	20
3 , 13	18248 18270	2 2	22	20
7 , 15	18340 18365	0 0	25	20

Table IV (continued)

v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$	v', v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
9 , 16	18354 18376	1 3	22	21	3 , 9	19047 19060	3 7	13	13
14, 18	18365 18384	0 6	19	25	0 , 7	19053 19067	8 6	14	13
1 , 11	18384 18402	6 3	18	19	2 , 8	19117 19127	3 3	10	13
12, 17	18426 18448	0 8	22	22	4 , 9	19169 19183	1 1	14	12
6 , 14	18426 18448	0 8	22	19	3 , 8	19246 19256	5 6	10	11
0 , 10	18448 18467	8 7	19	18	0 , 6	19256 19268	6 5	12	11
8, 15	18448 18467	8 7	19	19					
3 , 12	18448 18467	8 7	19	18	2 , 7	19320 19334	3 1	14	11
2 , 11	18519 18540	0 0	21	18	1 , 6	19389 19399	0 0	10	10
4 , 12	18577 18599	2 2	22	17	0 , 5	19459 19469	6 4	10	10
1 , 10	18583 18601	2 2	18	17	2 , 6	19523 19531	0 2	8	9
0 , 9	18650 18667	10 8	17	17	1 , 5	19593 19600	5 2	7	8
3 , 11	18650 18667	10 8	17	17	3 , 6	19650 19660	4 3	10	8
2 , 10	18721 18732	0 0	11	16	0 , 4	19665 19673	3 3	8	8
1 , 9	18784 18793	2 3	14	15	7 , 8	19730 19738	1 1	8	8
0 , 8	18850 18866	9 7	16	15	11, 10	19715 19724	0 1	9	10
3 , 10	18850 18866	9 7	16	15	1 , 4	19793 19805	5 3	7	7
1 , 8	18983 19003	0 1	14	20	3 , 5	19857 19865	0 0	8	6

Table IV (continued)

v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$	v' , v"	ν in cm^{-1}	I	$\Delta\nu_{obs}$	$\Delta\nu_{cal}$
0 , 3	19865	0	12	6					
	19877	3							
1 , 3	20005	5	5	5					
	20010	3							
11, 8	20116	3	10	7					
	20126	0							
9 , 7	20139	5	11	5					
	20150	?							
5 , 1	20936	4	5	3					
	20931	3							
9 , 3	20961	0	6	2					
	20955	0							
6 , 1	21054	0	8	4					
	21046	0							
13, 3	21290	?	8	2					
	21282	1							
11, 2	21350	2	7	4					
	21343	3							
10, 1	21472	1	12	6					
	21460	3							
8 , 0	21477	1	5	7					
	21472	1							
13, 2	21495	1	4	4					
	21491	\							

as well as in absorption, it is likely that the lower state of the system is the ground state of the molecule dissociating into Bi($^4S_{3/2}$) and Br($^2P_{3/2}$) atoms which are the ground states of bismuth and bromine atoms respectively.

The absorption spectrum obtained by Morgan shows that the band heads of this system converge rapidly and that the convergence limit lies somewhere in the region 4500 - 4570A where the absorption looks continuous. From the formula developed by him for the upper state of the system, he determined the convergence limit to be 4520A or 22120 cm^{-1}. This value which can be taken to be fairly accurate, represents the dissociation limit of the upper state as measured from the v" = 0 position of the ground state. The question arises whether this limit represents the dissociation limit into Bi($^4S_{3/2}$) + Br($^2P_{3/2}$) atoms or Bi($^4S_{3/2}$) + Br($^2P_{1/2}$) atoms. It was shown in the earlier chapter that the upper state of the analogous system in BiCl probably dissociates into Bi($^4S_{3/2}$)+Cl($^2P_{1/2}$) atoms and not into Bi($^4S_{3/2}$) +Cl($^2P_{3/2}$) atoms. Assuming this analogy, the upper state of the BiBr system can be taken to dissociate into Bi($^4S_{3/2}$) + Br($^2P_{1/2}$) atoms at 22120 cm^{-1}. Subtracting the doublet separation[3] of the normal bromine atom from this value, the dissociating limit for the ground state, which dissociates into Bi($^4S_{3/2}$) + Br($^2P_{3/2}$) atoms comes out to be 22120 - 3685=18435cm^{-1}. The coefficient of the cubic term in the expression for the lower state of the system in equation(I)has been so adjust-

ed that yields this value of 18435 cm^{-1} for the dissociation energy. The dissociation energies of the upper and lower states of the present BiBr system can thus be finally written as Do' = 22120 cm^{-1} and Do" = 18427 cm^{-1}

Electronic Transitions Involved.

As the present system of BiBr is taken to be most probably analogous to that of the BiCl system in the region 6170 - 4220 A , the discussion about the electronic transitions for BiCl given in earlier chapter will hold true for BiBr also. Thus the electronic transition involved in this band system of BiBr is probably

$$(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2\,(\omega\pi)^4\,(\upsilon\pi)\,(6\sigma)\,{}^3\Pi(0^+) \longrightarrow$$

$$(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2\,(\omega\pi)^4\,(\upsilon\pi)^2 \quad {}^3\Sigma^-(0^+)$$

where the $^3\Sigma^-(0^+)$ is the ground state dissociating into Bi($^4S_{3/2}$) + Br($^2P_{3/2}$) atoms and $^3\Pi(0^+)$ is the upper state dissociating into Bi($^4S_{3/2}$) + Br($^2P_{1/2}$) atoms.

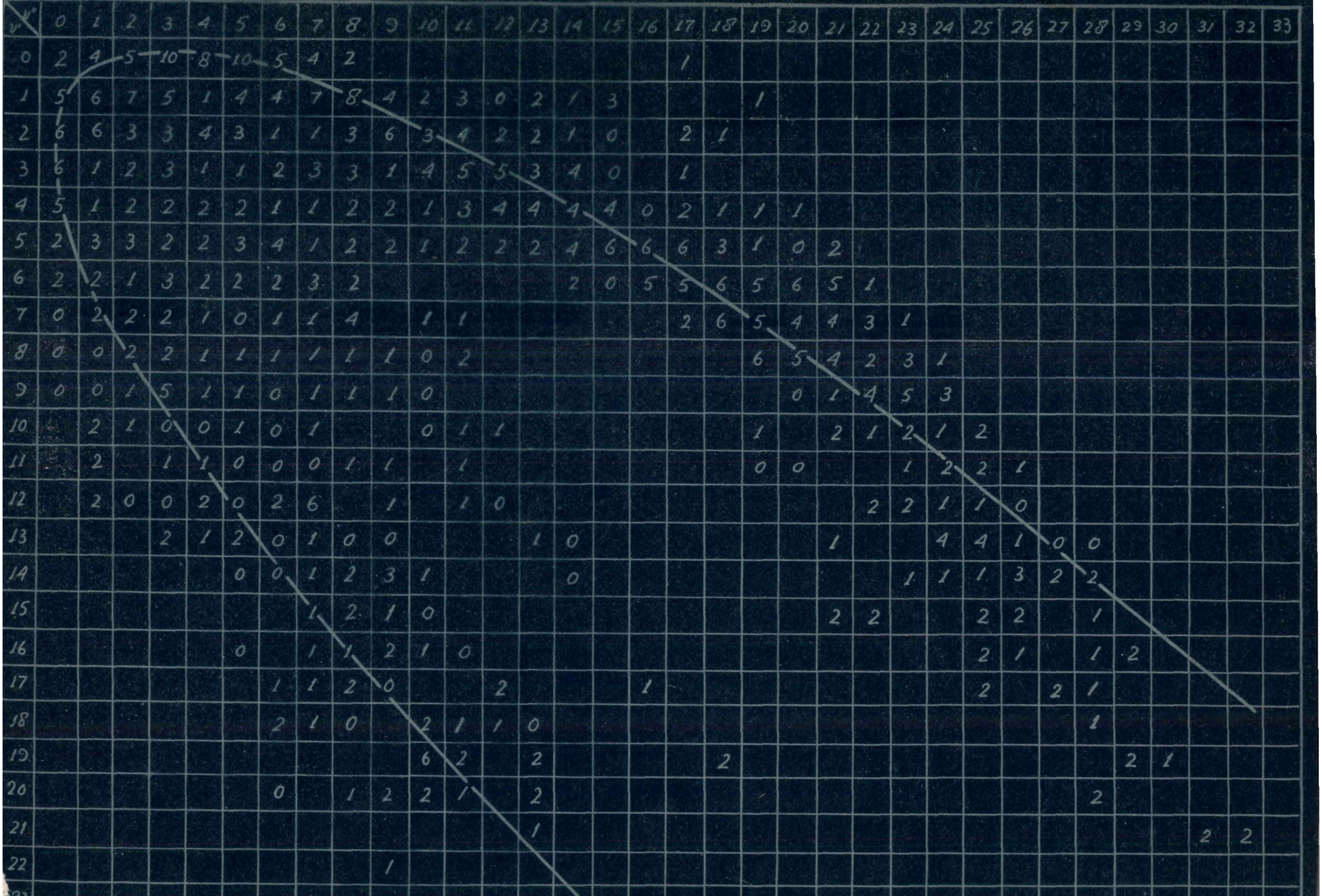
References.

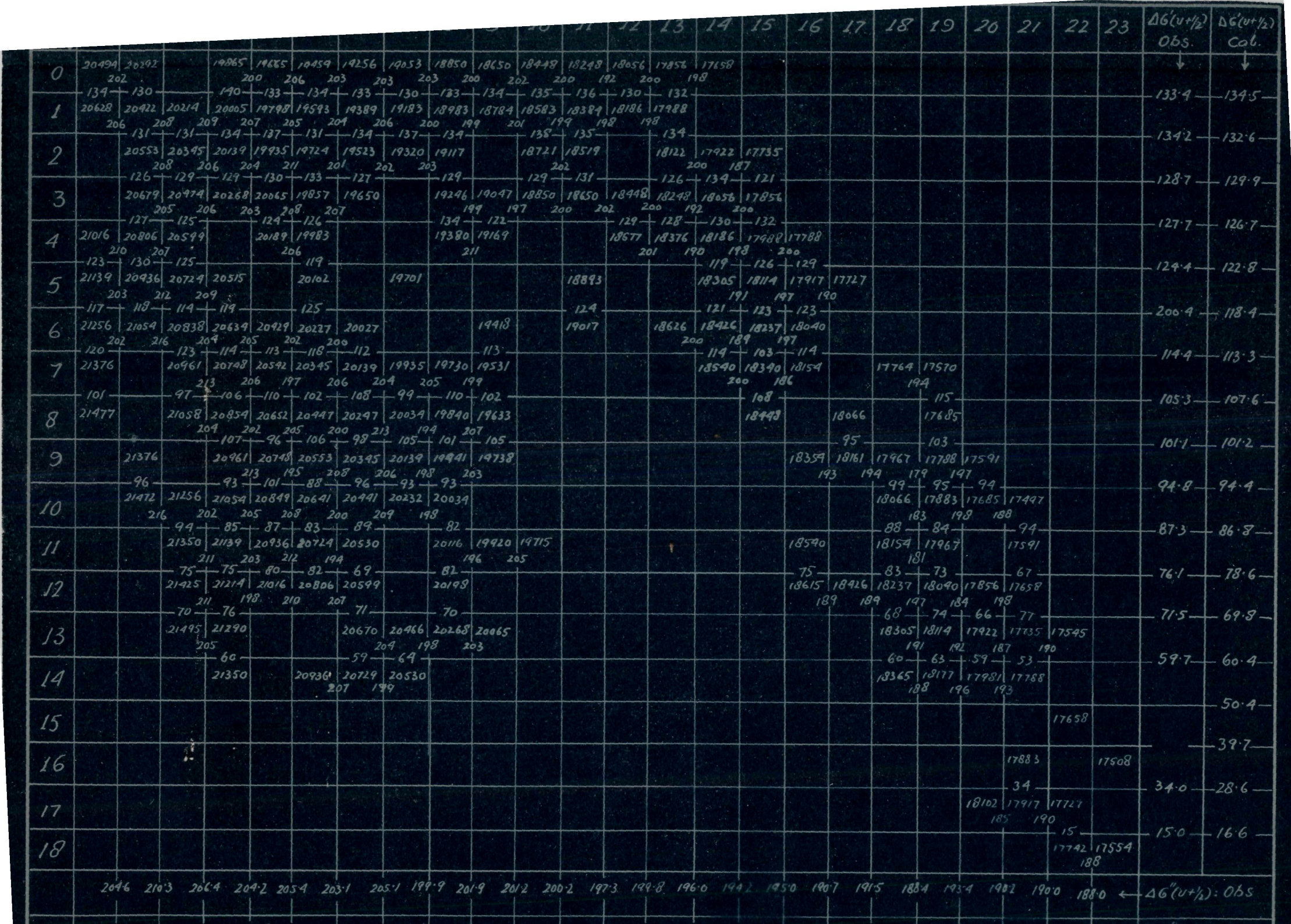
1. Morgan. Phys. Rev. (1936), 49, 41.
2. Howell and Rochester. Univ. Durham. Phil. Soc. Proc. (1934), 9, 126.
3. Turner. Phys. Rev. (1926), 27, 397.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
0	0	0		0	3	6	6	8	9	10	8	2	2	5	3									
1	0	2	4	5	5	4	0	1	0	2	2	6	4	5										
2		3	5	5	3	1	1	3	3		0	0		3	4	1								
3		2	5	0	0	0	4		5	8	9	10	8	2	2	5								
4	2	4	4		0	3			2	1			2	3	4	5	3							
5	2	4	0	1		2		1				2			0	3	4	6						
6	0	0	2	0	2	0	0			?		2		2	0	3	2							
7	1		0	2	3	5	5	1	1	2					0	0	1		2	2				
8	1		0	0	2	0	0	0	1	3						8		0		2				
9		1		0	2	3	5	5	0	1							1	6	3	4	4			
10		1	0	0	0	0	2	0	0										0	4	2	1		
11			2	2	4	0	0		3	1	0						0		1	3		4		
12			0	3	2	4	4		0								2	0	3	2	5	3		
13			1	?			2	2	0	0									0	3	4	1	0	
14				2		4	0	0											0	3	5	3		
15																							3	
16																						4		1
17																					2	4	6	
18																							6	2

TABLE III.

Intensity distribution and Franck-Condon Parabola for the bands in the system 6170-422A. of Biel




0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
ΔG(v+½) Obs.
ΔG(v+½) Cal.
133·4 134·5
134·2 132·6
128·7 129·9
127·7 126·7
124·4 122·8
200·4 118·4
114·4 113·3
105·3 107·6
101·1 101·2
94·8 94·4
87·3 86·8
76·1 78·6
71·5 69·8
59·7 60·4
50·4
39·7
34·0 28·6
15·0 16·6
204·6 210·3 206·4 204·2 205·4 203·1 205·1 199·9 201·9 201·2 200·2 197·3 199·8 196·0 194·2 195·0 190·7 191·5 188·4 193·4 190·2 190·0 188·0 ← ΔG''(v+½): Obs